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**THE EFFICACY OF CHITOSAN AND OTHER NATURAL
POLYMERS IN REMOVING COD, TSS, HEAVY METALS
AND PAHs FROM MUNICIPAL WASTEWATER AT DEER
ISLAND, MASSCHUSETTS**

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IN REMOVING COD, TSS, HEAVY METALS AND PAHs
FROM MUNICIPAL WASTEWATER AT DEER ISLAND, MASSACHUSETTS**

by
Susan Murcott and Donald R.F. Harleman
October, 1992

Table of Contents
List of Figures
List of Tables
Executive Summary

1. Introduction
 - 1.1 Background
 - 1.2 Coagulation and Flocculation
 - 1.3 Polymers and Polyelectrolytes
 - 1.4 Characteristics of Synthetic and Natural Polymers
 - 1.5 Favorable Environmental Characteristics of 3 Natural Polymers
2. Natural Polymer Jar Tests for COD and TSS Removal
 - 2.1 Previous Work
 - 2.2 Analytic Methods
 - 2.3 Jar Test Results for COD and TSS Removal
 - 2.31 Chitosan as a Primary Coagulant
 - 2.32 Chitosan as a Primary Coagulant + Moringa as a Coagulant Aid with or without a Flocculent
 - 2.33 Chitosan as a Coagulant Aid with and without a Flocculent
 - 2.34 Moringa as a Coagulant Aid/Flocculent
 - 2.35 Chitosan as a Coagulant Aid/Flocculent
 - 2.4 Summary
3. Jar Tests of Metals Removal
 - 3.1 Figures
 - 3.2 Summary
4. Polycyclic Aromatic Hydrocarbons (PAHs)
5. Sludge
6. Economic Analysis
7. References

Appendix A: Results of Chitosan Tests on Wastewaters
Appendix B: Solution Make-up Procedure
Appendix C: Jar Test Procedure
Appendix D: Jar Test Data Sheets
Appendix E: Batch Test Procedure for Deer Island
Appendix F: Raw Data -- TSS and COD
Appendix G: Raw Data -- Metals
Appendix H: PAH Analysis Procedure, PAH Raw Data
Appendix I: Relevant Economic Information

LIST OF FIGURES

- Figure 1: Chitosan as a Primary Coagulant - COD % Removal vs. Chitosan Concentration
- Figure 2: Chitosan as a Primary Coagulant - COD % Removal for Various Anionic Polymers at Deer Island 6/11/92
- Figure 3: Effect of Influent Concentration on COD % Removal - Chitosan as a Primary Coagulant
- Figure 4: Effect of Temperature on COD % Removal - Chitosan as a Primary Coagulant
- Figure 5: Effect of Mixing Speed on COD % Removal - Chitosan as a Primary Coagulant
- Figure 6: Effect of Mixing Time on COD % Removal - Chitosan as a Primary Coagulant
- Figure 7: Effect of Mixing and Settling Time on COD % Removal - Chitosan as a Primary Coagulant
- Figure 8: Comparison of Chitosan vs. Metal Salts as Primary Coagulants - TSS % Removal vs. Coagulant Concentration
- Figure 9: Comparison of Chitosan vs. Metal Salts as Primary Coagulants - COD % Removal vs. Coagulant Concentration
- Figure 10: Comparison of Chitosan & Ferric Chloride in Demineralized Water - COD Concentration vs. Coagulant Concentration
- Figure 11: Chitosan as a Primary Coagulant + *Moringa Stenopetala* as a Coagulant Aid with and without a Flocculent
- Figure 12: Chitosan as a Primary Coagulant + *Moringa Stenopetala* as a Coagulant Aid with Various Flocculents - COD % Removal
- Figure 13: Ferric Chloride + Chitosan as a Coagulant Aid with and without a Flocculent - COD % Removal vs. FeCl_3 Concentration
- Figure 14: Ferric Chloride + Chitosan as a Coagulant Aid with and without a Flocculent - COD % Removal vs. FeCl_3 Concentration
- Figure 15: Ferric Chloride + Chitosan as a Coagulant Aid with and without a Flocculent - COD % Removal vs. FeCl_3 Concentration
- Figure 16: Comparison of Chitosan vs. Various Synthetic Cationic Coagulant Aids in Removal of % COD
- Figure 17: Comparison of Chitosan and *Moringa* as Coagulant Aids - COD % Removal vs. FeCl_3 Concentration
- Figure 18: Comparison of 2 *Moringa* Species as Coagulant Aids - COD % Removal at Different FeCl_3 Concentrations
- Figure 19: Chitosan as a Flocculent - COD % Removal vs. Chitosan Concentration
- Figure 20: Aluminum Removal by 3 Primary Coagulants
- Figure 21: Chromium Removal by 3 Primary Coagulants
- Figure 22: Copper Removal by 3 Primary Coagulants
- Figure 23: Iron Removal by 3 Primary Coagulants
- Figure 24: Manganese Removal by 3 Primary Coagulants
- Figure 25: Silicon Removal by 3 Primary Coagulants

Figure 26: Chromium Removal by FeCl_3 and 3 Coagulant Aids
Figure 27: Copper Removal by FeCl_3 and 3 Coagulant Aids
Figure 28: Aluminum Removal by FeCl_3 and 3 Coagulant Aids

LIST OF TABLES

Table 1:	Some Natural and Synthetic Polymers for Wastewater Treatment
Table 2:	Chemical Characteristics of Some Natural and Synthetic Polymers
Table 3:	Comparison of Coagulants' Environmental Characteristics
Table 4:	Recommended Chemical Regimes at 4 Northeast Municipal Treatment Facilities
Table 5:	Recommend Chemical Regimes Using Chitosan for Gloucester, Massachusetts
Table 6:	Summary of Averaged Primary Coagulant Results
Table 7:	Summary of Averaged Coagulant Aid/Flocculent Results
Table 8:	PAH Testing Results - Batelle Ocean Science
Table 9:	PAH Testing Results - July 27, 1992
Table 10:	PAH Testing Results - August 12, 1992
Table 11:	Estimated Annual Sludge Production Summary
Table 12:	Liquid Process Operation and Maintenance Costs
Table 13:	Annual Operation and Maintenance Costs for 2 Chemical Options
Table 14:	Annual Sludge Quantity
Table 15:	Cost of Sludge Handling and Disposal - Deer Island Wastewater Sludge
Table 16:	Cost of Sludge Handling and Disposal - NRC
Table 17:	Sludge Handling and Disposal Operation and Maintenance Costs for 2 Chemical Treatment Options
Table 18:	Total Operation and Maintenance Cost Summary
Table 19:	4 Cases Showing a Variety of Chemical, Sludge Disposal and Cost Options

EXECUTIVE SUMMARY

A series of tests was conducted at the Deer Island Primary Treatment Plant during the spring and summer of 1992 to determine the efficacy of chitosan and other natural polymers as coagulants, coagulant aids and flocculents in wastewater treatment. Prior to this undertaking, as part of the MIT "Investigation of Chemically Enhanced Primary Treatment at the MWRA Project," the efficacy of metal salts and synthetic polymers had been studied at Deer Island. Those tests provided the standard against which to measure the viability of natural polymer use in municipal wastewater treatment. The major conclusions of the chitosan and other natural polymers study for Deer Island wastewater are as follows:

Chitosan as a Primary Coagulant: Chitosan as a primary coagulant gives good COD removal at influent concentrations above 300 mg/l. Under these optimal conditions, 5 mg/l chitosan can perform comparably with 40 mg/l metal salts, removing a maximum of 66% of COD. At lower influent COD values, chitosan performs inconsistently. Overall, COD removals with chitosan as a primary coagulant are not as good as with metal salts. On average, chitosan as a primary coagulant doubles the efficiency of the zero chemical test (which simulates conventional primary effluent), whereas metal salts triple the efficiency of the zero chemical test. The optimal dose of chitosan is 4 mg/l to 5 mg/l.

Chitosan as a Coagulant Aid: In 2-chemical systems, 2 mg/l chitosan as a coagulant aid/flocculent performs comparably with 0.2 mg/l of the anion #2540.

Natural Polymers Only: 5 mg/l chitosan + 1 mg/l to 2 mg/l *Moringa stenopetala* removes greater than 50% COD under high influent COD conditions.

Sludge Production: The optimal chemical dose of chitosan and *Moringa stenopetala* (5 mg/l chitosan, 1 mg/l to 2 mg/l *Moringa stenopetala*) will produce less sludge than the optimal dose of 40 mg/l to 50 mg/l ferric chloride or alum.

Metals Removal: Chitosan performs as well or better than either ferric chloride or alum as a primary coagulant in the removal of all metals tested. It can be used at very low concentrations of 4 mg/l to 6 mg/l. Chitosan as a primary coagulant successfully removes greater than 88% of chromium, zinc, copper, aluminum, and iron. In facilitating metals removal, chitosan can be used as a coagulant aid instead of as a primary coagulant if so desired.

PAH Removal: Either of 2 chemical regimes: ferric chloride plus chitosan as a coagulant aid/flocculent or ferric chloride plus the anion #2540 gave lower PAHs concentrations than those which occurred in the Deer Island effluent.

Economic Assessment: Chitosan is too expensive at the current market price and perhaps at the estimated "bulk" quantity price to be viable at this time as a treatment chemical in municipal wastewater treatment. However, chitosan has good market potential in those industrial and potable water treatment processes when it either generates an animal feed product, "soluble protein concentrate" or when it allows for the beneficial reuse of sludge that might otherwise require more costly disposal methods.

1. INTRODUCTION

1.1 Background:

With the increasing use of chemical coagulants to enhance wastewater treatment settling processes and the concomitant concerns about the environmental effects of chemical coagulant use and sludge production and reuse, the issues of chemical type and dose become important. The chemicals most commonly employed in wastewater treatment are metal salts: ferric chloride, aluminum sulfate, ferric sulfate, polyaluminum chloride; and synthetic organic polymers.

The use of organic polymers in coagulation has been studied and practiced since the late 1950s (Kawamura, 1976). Today, organic polymers, whether natural or synthetic, are of interest in water and wastewater treatment for the following reasons:

1. They are effective in very low dosages as compared with metal salts;
2. Low dosages of polymers reduces the volume of sludge produced;
3. Polymers improve the sludge dewatering process as compared with iron salts or alum (Kawamura, 1976);
4. They are generally more biodegradable than alum or ferric salt sludges and therefore ease sludge digestion by microorganisms (Kawamura, 1976).
5. They are non-corrosive and easy to handle.

The natural polymers examined in this study have some additional favorable characteristics:

1. They are a renewable resource;
2. They are biodegradable;
3. They are non-toxic.

The use of chitosan could mean that shellfish waste currently disposed of in landfills could be recycled to a useful purpose. The use of natural polymers derived from seeds of tropical trees could provide a nondestructive use for tropical species that could relieve the pressure to cut tropical trees. Unlike metal salts, certain natural polymers do not affect pH. For municipal agencies, the use of natural polymers generally could be very good from a public relations standpoint.

This report explores the viability of chitosan and other natural polymers in municipal wastewater treatment applications.

1.2 Coagulation and Flocculation:

The terms coagulation and flocculation have different meanings to different people and are frequently used

interchangeably. The Encyclopedia of Chemical Technology (1980) refers to the general, but not universal, acceptance of the equivalence of the words coagulation and flocculation and recommends that authors departing from this usage state their distinction clearly. The Encyclopedia goes on to enumerate the more common types of distinctions drawn between coagulation and flocculation as 1) based on mechanisms for destabilization of a suspension and/or type of aggregate formed, coagulation implying formation of compact aggregates and flocculation implying formation of loose or open networks aggregates, 2) based on chemical agents used, coagulation for inorganic materials and flocculation for organic polymers, 3) based on engineering process steps, coagulation representing conditioning the particles with the chemical agent and flocculation representing the mechanical particle transport step (collisions between conditioned particles) leading to aggregation, and 4) based on another engineering usage, coagulation representing the overall aggregation process and flocculation again representing the particle transport step.

In this report and following general usage, coagulation and flocculation will be used interchangeably, with coagulation considered as the all-encompassing term. However, following engineering practice, the terms primary coagulant, coagulant aid, and flocculent will be used to distinguish between steps in the chemical addition procedure.

A working definition of coagulation, following Amirtharajah and O'Melia (1990), is given below:

Coagulation encompasses all reactions, mechanisms, and results in the process of particle aggregation within a water being treated, including *in situ* coagulant formation (where applicable), chemical particle destabilization, and physical interparticle contacts.

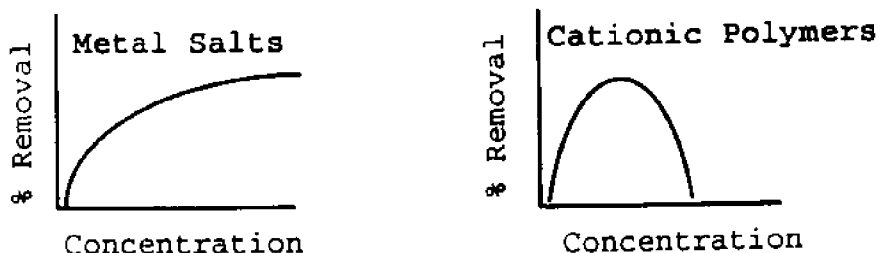
In wastewater treatment, in order for particles to come together, the surface potential of the particles needs to be destabilized. This is accomplished using a **primary coagulant** such as a multivalent metal ion or a relatively low molecular weight polymer. To accelerate this process, a **coagulant aid** may be used. Flocculation as a step in water and wastewater process design is the physical process of producing contacts by gentle stirring of chemically conditioned waters to enhance the grouping or agglomeration of colloidal particles into large voluminous flocs. A **flocculent** is the second (if no coagulant aid is added) or third (if a coagulant aid is added) chemical added in the chemical addition sequence.

In wastewater treatment, metal salts typically function as coagulants. Natural or synthetic polymers may be used as coagulants, coagulant aids and/or as flocculents. The logic of this chemical addition sequence is based on the understanding that coagulation of colloids requires the neutralization of electric charge before the suspension can be destabilized and

particles agglomerated. Conditioning chemicals with high electric charge densities are required. Because most particles found in nature (including wastewater particles) have a negative surface charge, they require positive conditioning chemicals: the hydronium ion (H_3O^+), metal cations (Ca^{+2} , Fe^{+2} , Fe^{+3} , Al^{+3}), and cationic polyelectrolytes to fulfill this service.

The closer the surface charge of a particle approaches zero, the more bridging becomes the important operator. Bridging is usually associated with the medium and high molecular weight polyelectrolytes and refers to the ability of the polymer to gather and hold the charge-neutralized fine flocs. Hydroxide flocs formed by metal salts are very effective charge destabilizers but only mildly effective bridgers. Cationic polyelectrolytes run from mild to strong charge neutralizers and strong to mild bridgers. That is to say, the charge neutralization and the bridging abilities of organic cationic polyelectrolytes run counter to one another.

When a metal salt is used alone as a primary coagulant, the performance curve levels off. The optimum dose is the lowest dose that will achieve the desired goal. When a cationic polymer is used alone as a primary coagulant, a distinct optimum dose and small effective dose range is found, after which performance deteriorates. The optimum dose is the dose at the peak of the performance curve. The sketch below shows this generalized performance trend.



In this study it was found that chitosan, in common with organic cationic polymers generally, has a small effective range. An overdose will have an adverse effect on coagulation.

Another key difference between metal salts and cationic polymers is their hydrolytic reaction with water. Metal salts undergo hydrolysis when added to water. The hydrolytic reaction produces hydroxocomplexes, such as $Fe(OH)^{2+}$, $AlOH^{2+}$, $Fe(H_2O)_3$, $Al(H_2)_6$. The formation of hydrolytic products occurs in a short period of less than 1 second. The hydroxocomplexes readily adsorb to colloidal particles and cause destabilization of electrical charge. The hydrolytic products are quickly polymerized through hydrolytic reactions.

When cationic polymers such as chitosan are added to wastewater, hydrolytic reactions do not occur. Instantaneous mixing is not critical and the rate of colloidal adsorption is much slower. Mixing time is between 2 to 5 seconds as opposed to being nearly instantaneous.

1.3 Polymers and Polyelectrolytes:

Polymers are long chain organic molecules formed by the joining together (polymerization) of simple, basic chemical units (monomers) intoidered in this study are given in Table 2:

TABLE 2
CHEMICAL CHARACTERISTICS OF SOME SYNTHETIC AND NATURAL POLYMERS

Chemical	% Solids	Molecular Weight (Daltons)	Charge Density (Mol %)	Viscosity (Centipoise)
Cationic Polyacrylamide Delta 6395 Delta 7394	38.2 40	8M 14M	60 60	
Anionic Polyacrylamide Delta 2540	0.75	20M	40	
Chitosan	100	161 - 2M (ave. 200,000)		2000
Moringa Oleifera		6,000 - 16,000		
Moringa Stenopetala		8,000		

As a general rule, natural polymers have relatively low molecular weights. We see from this table that the natural polymers: chitosan, *Moringa oleifera* and *Moringa stenopetala* all have molecular weights under 200,000. In contrast, the synthetic cationic and anionic species range in molecular weights from medium to very high.

In this study it was found that of the many natural polymers tested, 3 of them: chitosan, *Moringa stenopetala* and *Moringa oleifera*, showed the greatest promise for municipal wastewater treatment applications. Because *Moringa stenopetala* seemed to outperform *Moringa oleifera*, it was the *Moringa* species which was most extensively tested. A description of these 3 natural polymers follows:

Chitosan:

Chitosan is a natural polymer derived from chitin, the organic exoskeletal of crustacea such as crabs, shrimp, prawns, and lobster. The amount of chitin in crustacean shells varies from about 20% for heavily armored shells such as crabs, to about

35% to 40% of the weight of shrimp shells. The remaining fractions consist lime and protein. Chitosan is produced from the partial deacetylation of chitin in concentrated alkali solutions at 135 to 150 degrees Centigrade. Chitin is isolated by washing out the lime with dilute hydrochloric acid and the protein with a dilute alkali. The chitin is then further hydrolyzed to turn it into chitosan.

Chitosan is a polysaccharide composed of poly-N-acetylglucoamine units, linked by beta 1-4 glycosidic bonds into a linear polymer. It is a cationic polyelectrolyte, a salt of a weak base. Molecular weight of the monomer is 161 Daltons; undenatured chitosan can be 2×10^6 Daltons. Viscosity is about 2,000 centipoise.

Stability: Chitosan has been found to be stable indefinitely in dilute solutions, with no signs of bacterial activity or degradation in a 5 year old solution (Kawamura, S., 1981).

Moringaceae: is a single-genus family of 14 known species, indigenous to Africa, India, Madagascar, and Arabia. Some of these 14 species include *Moringa peregrina* (Egypt), *Moringa stenopetala* (Kenya), *Moringa longituba* (Somalia), *Moringa drouhardii* (Madagascar), *Moringa ovalifolia* (Namibia), *Moringa oleifera* (sub-Himalayan India and Pakistan), *Moringa concanensis* (India and Pakistan). Half of these species are relatively common. Because of its many uses (fuel, foodstuffs, vegetable oil, medicines) *Moringa oleifera* is the *Moringa* species which is currently most abundant throughout the entire tropical belt.

Attempts to isolate *Moringa* flocculents showed that they are basic polypeptides with molecular weights ranging from 6,000 to 16,000 Daltons. (Jahn, 1988)

Stability: *Moringa* seed suspensions yielded turbidity removal of the same magnitude as fresh suspensions for about 3 days (Jahn, 1988).

Moringa oleifera: Folkhard reports the results of 3 separate chemical analyses of *Moringa oleifera* seeds (Folkhard, 1986). In the first, the weight ratio of seed to skin is reported as 65:35. On a percentage of total weight basis the following pertains: calcium: 0.18, phosphorus: 0.69, protein 36.0, fat 32.09. In the second, moisture: 4%, crude protein 38.4%, oil, 34.7%, N-free extract 16.4%, fibre 3.5% and ash 3.2%. The active ingredient is thought to be contained in the N-free extract. The third study the active ingredient was identified as amino acids with arginine present at a concentration of 14.8 Mol%.

Moringa stenopetala: has proven effective in clarifying water over a wide range of turbidities. It is a particularly attractive type of *Moringa* because it has a significantly higher average yield than that of *Moringa oleifera* (Folkhard, G.K., 1986). Molecular weight is about 8,000 Daltons.

1.5 Favorable Environmental Characteristics of the 3 Natural Polymers Tested:

The 3 natural polymers just described have the favorable environmental characteristics of renewability, non-toxicity, and biodegradability.

Renewability: Chitosan is a modified form of chitin, the second most abundant natural polymer after cellulose. Chitosan is made from shellfish waste. The 2 *Moringa* seeds are from a species of tree abundant in the tropics.

Toxicity: Under its former chemical additives advisory program, the U.S. EPA created a list of products that many states used and included a maximum dosage for each product. The maximum dose of chitosan for drinking water treatment was given as 10 mg/l. *Moringa oleifera* seeds have been shown to be non-toxic (Barth, W.H. et.al., 1982; Folkhard, 1986). Neither did acute and chronic toxicity tests on rats with *Moringa oleifera* and *Moringa stenopetala* seed in dosages of 50 and 500 mg/kg body weight show any sign of toxicity. Powdered seed kernels in concentrations up to 1000 mg/l had no detectable mutagenic effect on salmonella tester strains. (Jahn, 1988)

Biodegradability: Natural polymers generally are considered to be biodegradable (Grayson, 1984).

2.0 NATURAL POLYMER JAR TESTS OF COD AND TSS REMOVAL

A series of tests of the efficacy of chitosan and other natural polymers was undertaken from April through August, 1992 at the existing ("old") Deer Island primary treatment plant in Boston, Massachusetts. The purpose of these tests was to investigate the feasibility of using chitosan and other natural polymers in wastewater treatment through 3 phases of work:

- 1) Jar tests of natural polymer performance in removing conventional pollutants (i.e. chemical oxygen demand (COD) and total suspended solids (TSS)) from wastewater;
- 2) Jar tests of natural polymer efficacy in removing heavy metals from wastewater;
- 3) Batch tests of natural polymer performance in removing polycyclic aromatic hydrocarbons (PAHs) from wastewater.

Jar tests and batch tests were the vehicles by which the efficacy of chitosan and other natural polymers as primary coagulants, coagulant aids, or flocculents were examined. Samples were analyzed at the Deer Island site and/or at Parsons Laboratory for COD, TSS heavy metals and PAHs.

2.1 Previous Work:

Over the past 4 years, extensive experience with testing chemical addition in municipal wastewater treatment had been gained by MIT researchers through lab-scale and full-scale experimentation at primary treatment plants in Salem, MA, Gloucester, MA, Boston, MA, and New York City (Morrissey et.al. 1992; Murcott and Harleman, 1992). Appropriate chemical regimes were developed for each facility using metal salts and synthetic polymers. Table 4 gives recommended chemical regimes for each facility:

TABLE 4
RECOMMENDED CHEMICAL REGIMES
AT 4 NORTHEAST MUNICIPAL TREATMENT FACILITIES

Plant	Coagulant	Coagulant Aid	Flocculent
Salem, MA (SESD)	40 mg/l Alum	0.2 mg/l cation	0.5 mg/l anion
Gloucester, MA (GWPCF)	40 mg/l Ferric Chloride		0.5 mg/l anion
Boston, MA (Deer Island)	40 mg/l Ferric Chloride		0.2 mg/l anion
New York, N.Y. (Owls Head)	15-50 mg/l Ferric Chloride		0.35 mg/l anion

In addition, chemically enhanced primary treatment tests at the Gloucester Water Pollution Control Facility (GWPCF) during 1991, in work supported by MIT Sea Grant, concluded that 2 different chemical regimes using chitosan were feasible for increasing the removal efficiency of the conventional pollutants TSS and five day biochemical oxygen demand (BOD5) or COD at that plant (Murcott, S. and Harleman, D.R.F., 1992). Table 5 presents these regimes:

TABLE 5
RECOMMENDED CHEMICAL REGIMES USING CHITOSAN
FOR GLOUCESTER, MASSACHUSETTS

Coagulant	Coagulant Aid	Flocculent
5 - 15 mg/l chitosan	5 mg/l cation	0.5 -1.5 mg/l anion
10 - 20 mg/l FeCl ₃	5 - 10 mg/l chitosan	0.5 mg/l anion

Past work also included a literature review of previous chitosan testing in wastewater applications by other researchers. These results are summarized in Appendix A.

The first phase of new work at Deer Island was to test the chitosan regimes developed at GWPCF against Deer Island wastewater conditions in order to verify and extend the understanding of the effect of natural polymers in wastewater treatment.

2.2 Analytic Methods

Chitosan and other natural polymers were tested as primary coagulants, as coagulant aids, and as flocculents. Chemical solutions were made up in advance according to procedures described in Appendix B. A standard jar test procedure had been established in previous testing and is given in Appendix C. The chief analytic tool used to determine the performance of a given chemical in its ability to remove conventional pollutants was COD. COD was chosen for 2 reasons: its ability to correlate with BOD5 and the short analysis time of COD as compared with BOD5. The HACH COD method, an EPA approved method, was the major analytic procedure used. Previous experience at Deer Island and elsewhere had shown that for high COD removal to occur, high TSS must also occur (Morrissey et.al., 1992). TSS tests were also performed as a supplement to COD tests.

The qualitative parameter of visual observation was also used as a means of screening chemical types and dosages prior to undertaking COD or other quantitative analyses. Visual observations for all runs were recorded on Jar Test Data Sheets (Appendix D).

Visual observation results led to the screening out from further investigation of a number of natural polymers: almonds, oak seeds, 2 types of carrageenan: Purgell 400 and Bengel WG 2000, alginate. Seawater and sodium potassium as a base to enhance chitosan effectiveness were also tried and screened from further investigation.

2.3 Jar Test Results for COD and TSS Removal:

The first set of results are averages of all jar test samples over the entire test period. They show that the zero chemical regimes gave a 17 % COD removal, the primary coagulant regimes using chitosan gave a 34% COD removal (exactly double the efficiency of the zero chemical jar) and the metal salt regimes generally gave COD removals that were triple the efficiency of the zero chemical regimes. These data also show that ferric chloride and alum performed almost identically at the 2 metal salt test concentrations of 20 mg/l and 40 mg/l. This first set of averaged results is presented in Table 6.

TABLE 6
SUMMARY OF AVERAGED PRIMARY COAGULANT RESULTS

	Concentration (mg/l)	% COD Removal	# of Samples Tested
Raw Influent	265		16
Zero Chemical (= Effluent)	219	17	6
5 mg/l Ch + 0.2 mg/l #2540	175	34	16
20 mg/l FeCl ₃ + 0.2mg/l #2540	141	47	4
40 mg/l FeCl ₃ + 0.2mg/l #2540	109	59	4
20 mg/l Alum + 0.2 mg/l #2540	138	48	2
40 mg/l Alum + 0.2 mg/l #2540	110	58	2

The second set of averaged results compares chitosan with a synthetic anionic polymer as a coagulant aid/flocculent in a 2-chemical system. Ferric chloride is the primary coagulant and either chitosan or the anion #2540 is the second chemical added (referred to here as the coagulant aid/flocculent to indicate that this is a 2-chemical rather than a 3-chemical system). The difference in dose between chitosan and the anion #2540 (2 mg/l versus 0.2 mg/l) was chosen because these were considered the optimal doses. Table 7 shows us that chitosan performs just slightly better than the anion #2540 with 20 mg/l ferric chloride.

TABLE 7
SUMMARY OF AVERAGED COAGULANT AID/FLOCCULENT RESULTS

	Concentration (mg/l)	% COD Removal	# of Samples Tested
Raw Influent	265		16
Zero Chemical (= Effluent)	219	17	6
20 mg/l FeCl ₃ + 2 mg/l Ch	129	51	3
20 mg/l FeCl ₃ + 0.2mg/l #2540	141	47	4

The figures presented and discussed below give the results of the first phase of jar testing in which COD and TSS removals were evaluated.

2.31 Chitosan as a Primary Coagulant

Figure 1. COD % Removal vs. Chitosan Concentration: On a number of days throughout the research period, chitosan was tested as a primary coagulant. Experience at the Gloucester Water Pollution Control Facility had shown that chitosan as a primary coagulant could be used in dosages between 5 mg/l and 15 mg/l, a lower dose range than is typical for metal salts. At Deer Island, chitosan as a primary coagulant was tested in a range of concentrations from 1 mg/l to 16 mg/l. Figure 1 presents all those COD % removal results where chitosan was evaluated as a primary coagulant and 0.2 mg/l of the anion #2540 was used as a coagulant aid/flocculent in a 2-chemical system.

Figure 1 shows that the optimal chitosan dose for Deer Island wastewater is between 4 mg/l and 5 mg/l when chitosan is used as a primary coagulant. COD removal efficiency deteriorates when chitosan concentrations greater than 5 mg/l are used. The figure also shows that there is a lot of variability in chitosan's performance as a primary coagulant, i.e., it does not perform with consistency. The 2 data points that show COD % removal greater than or equal to 40% occurred when influent concentrations were greater than 300 mg/l.

Figure 2. COD % Removal for Various Anionic Polymers: As shown in Figure 2, 5 mg/l of chitosan was tested with different anionic flocculents in doses of 0.2 mg/l and 0.5 mg/l. The chief difference between the anionic polymers was their charge mole percent. With dosages of 0.2 mg/l, the anionic polymers #2540 and L-285 performed more or less identically. With the higher dose of 0.5 mg/l, #2540 outperformed the other polymers tested. Although several of the polymers performed better than #2540 with the lower dose of 0.2 mg/l, we decided to carry out future tests with #2540 as the standard because it performed more or less the same as other synthetic flocculents and because there was a good data base of information for its performance at Deer Island. Figure 2 is one of several examples showing that relatively high COD removals (such as in Figure 1 for the 6/11/92 data point) are not isolated results, but borne out in subsequent tests.

Figure 3. Effect of Influent Concentration on COD % Removal: Figure 3 shows the effect of influent concentration on removal efficiency. Influent COD concentrations at Deer Island are typically around 250 mg/l. At these relatively low influent COD concentrations, chitosan performs poorly as a primary coagulant. Comparing chitosan performance with the 2 zero chemical data points, chitosan does not show any improvement in the first instance and is 23 percentage points higher in the second instance. Chitosan does, however, perform well as a primary coagulant at relatively higher influent COD concentrations, i.e. those greater than 300 mg/l.

Figure 4. Effect of Temperature on COD % Removal: Figures 4 examines the effect of temperature on COD removal efficiency when chitosan is used as a primary coagulant. Depending on the season, Deer Island influent wastewater temperature ranges from 12 to 20 degrees Centigrade. Because all chitosan testing took place during the spring and summer when the wastewater temperature was at the high end of its range, this test was designed to show the efficiency that could be expected to occur over the normal annual temperature range. The test showed that chitosan performed best in higher temperature wastewater. This is a predictable result, as warmer water enhances the speed of chemical reactions.¹

Figure 5. Effect of Mixing Speed on COD % Removal: Figures 5 presents the effect of mixing speed on COD removal efficiency when chitosan is used as a primary coagulant. The standard jar test procedure (see Appendix B) was altered in this test. Where typically, the coagulant is added, and after initial rapid mixing, it is stirred at a constant 60 rpm for 2 minutes, in this test, the speed of constant stirring was varied from 20 rpm to 100 rpm in increments of 20 rpms. Figure 5 shows that the highest mixing speed of 100 rpm gives the best results.

Figure 6. Effect of Mixing Time on COD % Removal: Figures 6 examines the effect of mixing time on COD removal efficiency when chitosan is used as a primary coagulant. The standard jar test procedure (see Appendix C) was altered in this test. Where typically, the coagulant is added, and after initial rapid mixing, it is stirred at a constant 60 rpm for 2 minutes, in this test, the mixing time of this stirring phase was varied from between 1 to 9 minutes in each of 6 jars. Figure 6 shows that the shorter mixing times of 0.5 to 3 minutes give little improvement in COD performance. However, the longest mixing time of 9 minutes gives a significantly better result.

Figure 7. Effect of Mixing Time and Settling Time on COD % Removal: Building on the lessons gained from the previous test, Figures 7 examines the characteristics of mixing time and settling time on COD removal efficiency when chitosan is used as a primary coagulant. Two jars from the previous experiment were sampled in 2 ways: each were sampled after the standard 5 minute settling period and each were sampled and analyzed after 1 hour of settling time. The jar mixed for 4 minutes (see Figure 6) showed better performance with 5 minute settling than with 1 hour settling. The jar mixed for 9 minutes showed the opposite -- better performance with 1 hour settling than with 5 minutes settling. No conclusions can be drawn.

¹ The same temperature effects of higher removal with higher temperature has been observed with metal salts and also with natural seed polymers (Folkhard, 1986).

Figure 8. Comparison of Chitosan and Metal Salts as Primary Coagulants -- TSS % Removal vs. Coagulant Concentration:

A comparison of the TSS removal efficiency of chitosan and metal salts as primary coagulants took place on 2 different test days. Chitosan was tested in concentrations ranging from 1 to 16 mg/l. Ferric chloride were tested in concentrations ranging from 5 to 80 mg/l and alum was tested at 20 and 40 mg/l. Figure 8 shows several important results: 1) for concentrations of 30 mg/l and greater, the metal salts FeCl_3 and alum outperform chitosan as a primary coagulant; 2) alum performed better than ferric chloride at 20 and 40 mg/l; 3) chitosan performed comparably with ferric chloride in concentrations of 5 mg/l.

Figure 9. Comparison of Chitosan and Metal Salts as Primary Coagulants -- COD % Removal vs. Coagulant Concentration:

A comparison was made of COD removal efficiency of chitosan and metal salts as primary coagulants. Chitosan was tested in concentrations from 0 mg/l to 6 mg/l. Ferric chloride and alum were tested at 20 mg/l and 40 mg/l. Figure 9 shows that chitosan gives poor COD removals relative to either of the metal salts tested and does not do much better than the zero chemical test in the ferric chloride or alum run. The low influent COD concentration of 232 mg/l should be noted.

Figure 10. Comparison of Chitosan and Ferric Chloride as Primary Coagulants in Demineralized Water -- COD % Removal vs. Coagulant Concentration: Tests of chitosan and ferric chloride as primary coagulants in demineralized water show that increasing concentrations of chitosan increased COD concentrations. This is expected. An organic polymer such as chitosan should add to the organic (COD) concentration. Note, however, that dosages of 10 mg/l and 25 mg/l chitosan are 2 and 5 times the optimal chitosan dosages respectively. Chitosan is not effective and would not be used in these high concentrations.

2.32 Chitosan as a Primary Coagulant + Moringa as a Coagulant Aid, with and without Synthetic Flocculents

Figure 11. COD % Removal vs. Moringa Stenopetala Concentration:

This figure shows that 5 mg/l chitosan as a primary coagulant plus zero or small doses of *Moringa stenopetala* as a coagulant aid plus the flocculent #2540 achieves very good COD removal of between 48% and 64%. Results represent 2 different test samples from the same day (6/11/92), both of which had higher than normal

influent COD concentrations.² On 6/24/92 (not shown in Figure 11), a synthetic flocculent offered little additional improvement in COD removal at a *Moringa stenopetala* concentration of 2 mg/l. These high COD removals are achieved using a natural polymer regime plus a synthetic flocculent with a small overall chemical dose. Figure 12 confirms this result.

Figure 12. COD % Removal vs. Anionic Flocculent Type and Concentration: This figure shows some of the best COD removal results obtained with natural polymers: 5 mg/l chitosan and 1 mg/l *Moringa stenopetala* tested with 0.2 mg/l of the synthetic flocculents #2540 or L-285 achieved over 60% COD removal. Both of the synthetic flocculents are 40 mole charge %.

2.33 Chitosan as a Coagulant Aid:

Figure 13, 14 & 15: Ferric Chloride + Chitosan as a Coagulant Aid with and without a Flocculent; COD % Removal vs. FeCl₃ Concentration All 3 of these figures consider the efficacy of chitosan as a coagulant aid with and without a flocculent. Figure 13 indicates that when the ferric chloride concentration is 20 mg/l, a 0.2 mg/l dose of chitosan (with flocculent) does best, a 2 mg/l dose of chitosan (with flocculent) does second best, and a 2 mg/l dose of chitosan (without flocculent) does least well. This result suggests using a lower dose of chitosan with a synthetic polymer. Figure 14 suggests that 2 mg/l chitosan plus 0.2 mg/l of a flocculent usually performs better than chitosan without the flocculent, but this is not a consistent result (see ferric chloride concentrations of 25 mg/l and 35 mg/l). Figure 15 indicates that 20 mg/l ferric chloride plus #2540 alone performs significantly better than 20 mg/l ferric chloride plus chitosan alone. This result suggests that chitosan as a coagulant aid/flocculent does not improve on the effect of the synthetic polymer without the chitosan.

Figure 16. Comparison of Chitosan and Various Synthetic Coagulant Aids. COD % Removal vs. Ferric Chloride Concentration: Tests performed at Deer Island in the winter of 1991-1992 on the performance of a wide range of synthetic cationic polymers provides a basis for comparison with chitosan as a coagulant aid. In the winter of 1991-1992, 5 mg/l synthetic polymers were tested with 40 mg/l ferric chloride and with 0.5 mg/l of #2540.

² In water quality tests of *Moringa stenopetala* and/or *Moringa oleifera*, Sutherland (undated) and Jahn (1988) found that both seed types were effective in high initial turbidities, but observed problems with turbidity removal at low initial turbidities. Jahn concluded that at low turbidities, twice as much *Moringa oleifera* as of alum was needed to obtain the same residual turbidity.

In the summer of 1992, 2 mg/l chitosan was tested over a range of ferric chloride concentrations, without a flocculent. Ferric chloride in concentrations ranging from 15 to 30 mg/l with 2 mg/l chitosan generally performed as well or better than 5 mg/l of any synthetic polymer and 0.5 mg/l of a flocculent.

2.34 Moringa as a Coagulant Aid/Flocculent

Figure 17: Comparison of Chitosan and Moringa Stenopetala as Coagulant Aids/Flocculents; COD % Removal vs. Ferric Chloride Concentration: This figure indicates that chitosan and *Moringa stenopetata* in concentrations of 2 mg/l perform more or less identically as coagulant aids/flocculents at 10, 15, 20, 25 and 30 mg/l ferric chloride. At 30 mg/l of ferric chloride, the use of a flocculent (as the 3rd chemical in a 3 chemical regime) does not consistently provide additional COD removal compared to using chitosan or *Moringa* as a coagulant aid (2nd chemical in a 3 chemical regime) without the flocculent.

Figure 18: Comparison of 2 Moringa Species as Coagulant Aids
Figure 18 compares 2 species of *Moringa* as coagulant aids, with and without the use of a synthetic flocculent. *Moringa stenopetala* performs better than *Moringa oleifera* and it does better without a synthetic polymer than with one.

2.35 Chitosan as a Coagulant Aid/Flocculent

Figure 19: COD % Removal vs. Chitosan Concentration:
Figure 19 shows that in 2-chemical regimes, 0.2 mg/l of the anionic polymer #2540 gives the same result as when 2 mg/l chitosan is used as a coagulant aid/flocculent. Dosages less than 2 mg/l chitosan and the higher dose of 5 mg/l chitosan all show poorer COD removal efficiency.

2.4 Summary

The following points summarize the COD and TSS jar test performance of chitosan and other natural polymers:

- 1) Chitosan as a primary coagulant gives good COD removal at influent concentrations above 300 mg/l. Under these optimal conditions, 5 mg/l chitosan can perform comparably with 40 mg/l metal salts, removing a maximum of 66% of COD. At lower influent COD values, chitosan performs inconsistently. Overall, COD removals with chitosan as a primary coagulant are not as good as with metal salts. On average, chitosan as a primary coagulant doubles the efficiency of the zero chemical test (which simulates conventional primary effluent), whereas metal salts triple the efficiency of the zero chemical test. The optimal dose of chitosan is 4 mg/l to 5 mg/l.
- 2) When chitosan is used as a primary coagulant in a 2 chemical regime with an anionic polymer, a polymer of high mole charge percent such as Delta #2540 or L-285 performs best. 0.2 mg/l is an appropriate concentration for the synthetic polymer.
- 3) Chitosan as a primary coagulant achieves its best results with: a) high mixing speeds of 100 rpm during the initial stirring phase; b) warmer wastewater temperatures of 20 degrees Centigrade; and c) longer mixing times of 9 minutes.
- 4) Chitosan, in common with organic cationic polymers generally, has a small effective dose range. An overdose will have an adverse effect on coagulation.
- 5) 5 mg/l chitosan + 1 mg/l to 2 mg/l *Moringa stenopetala* removes greater than 50% COD under high influent COD conditions.
- 6) In 2-chemical systems, 2 mg/l chitosan as a coagulant aid/flocculent performs comparably with 0.2 mg/l of the anion #2540.
- 7) When used as a coagulant aid, chitosan or either of 2 *Moringa* species perform more or less comparably in terms of COD removal.
- 8) The low overall chemical dose of chitosan and other natural polymers (4 to 5 mg/l for primary coagulants, 1-2 mg/l for coagulant aids/flocculents) would produce less sludge than the optimal dose of 40 mg/l to 50 mg/l for the metal salts ferric chloride or alum.

3. JAR TESTS OF METALS REMOVAL

Metals testing and analysis took place during June and July. Two-chemical regimes were studied. Testing regimes included ferric chloride, alum or chitosan as primary coagulants with the anionic polymer #2540; and ferric chloride or alum as a primary coagulant with chitosan or *Moringa* as a coagulant aid/flocculent. Jar tests samples were analyzed using inductively coupled plasma (IPC). Each sample was analyzed for 14 metals: chromium, cadmium, lead, arsenic, zinc, copper, aluminum, barium, iron, silicon, titanium, cobalt, nickel and manganese. Of the 14 metals tested, 9 metals were detected in the influent samples: chromium, zinc, copper, aluminum, barium, iron, silicon, manganese, and nickel. Cadmium, lead, and arsenic were detected in spikes only; titanium and cobalt were not spiked. Because nickel was not detected in the jar test samples (except in the spikes), only 8 metals were detected in both the influent and jar test samples. It is these 8 metals that are included in the analysis that follows.³

Duplicates were run on the influent. Spikes of chromium, cadmium, lead, arsenic, zinc, copper, iron, and nickel had reasonable recovery (i.e. high concentrations for that metal). Detection limits vary slightly for each element and are given in Appendix G. The ICP gives a margin of error of plus or minus 10 % and results up to and including the detection limit are considered valid. Five blanks were run and the average of those 5 blanks is shown in Appendix G. All metals concentration data is presented with the blank already subtracted.

3.1 Figures:

The following figures detail the performance of the various chemical regimes in the removal of 8 metals:

Figures 20, 21, 22, 23, 24 and 25: These figures show chitosan's success as a primary coagulant in achieving high removals of the metal under investigation at low dosages of 4 mg/l and 6 mg/l.

Figures 26, 27, and 28: This set of figures compares ferric chloride as a primary coagulant and 3 different coagulant aids/flocculents. The coagulant aid/flocculents are chitosan or *Moringa stenopetala*. The natural polymers, in concentrations of 2 mg/l, are compared with 0.2 mg/l #2540. These figures show that the 2 natural polymers used as coagulant aid/flocculents remove more chromium and about the same amount of copper and aluminum as does ferric chloride with #2540.

³ In recent years, the Deer Island municipal wastestream has had high concentrations of copper, lead and zinc. Copper and zinc were detected in these samples, lead was not.

3.2 Summary:

A summary of the findings include:

- * Chitosan performed well both as a primary coagulant and as a coagulant aid/flocculent in metals removal;

- * Very low concentrations of 4 mg/l and 6 mg/l of chitosan performed as well or better than either ferric chloride or alum as a primary coagulant in the removal of all metals for which results were obtained;

- * Chitosan as a primary coagulant successfully removed greater than 88% of chromium, zinc, copper, aluminum, and iron.

- * *Moringa* performed comparably to chitosan as a coagulant aid/flocculent in metals removal;

- * Aluminum removal was negative when alum was the primary coagulant; iron removal was low but positive, between 10% and 30%, when ferric chloride was the primary coagulant;

- * Ferric chloride contained high levels of manganese resulting in negative removals of manganese for all tests involving ferric chloride;

- * About 40% of barium was removed from all samples, regardless of chemical regime;

- * Silicon was barely removed by any chemical regime. However, chitosan was somewhat more successful at silicon removal than either ferric chloride or alum;

4. POLYCYCLIC AROMATIC HYDROCARBON (PAH) TESTING

Polycyclic aromatic hydrocarbons (PAHs) are a class of compounds containing 2 or more fused rings, at least 1 of which is a benzene ring. The best-known of these compounds is naphthalene, an important component of mothballs. Many of these compounds are found in crude petroleum and coal tar. Some of these compounds with the larger numbers of benzene rings are powerful carcinogens.

PAHs are formed from any hydrocarbon combustion process and also are released from oil spills. The less efficient the combustion process, the more likely a higher emission. Major stationary sources include heat and power generation, refuse burning, industrial activity, and coke ovens. Transportation sources represent only 1% of emitted PAHs nationally, yet they may approach 50% of the overall inventory in urban areas (Sittig, 1985).

Because of the large number of sources, PAHs are widely distributed in the environment and can be present in municipal wastewater. In wastewater, PAHs tend to associate with particles. Because of their association with particles, it was anticipated that the increased removal of COD and TSS through chemical coagulation would also increase the removal of PAHs. The purpose of testing PAHs at Deer Island was to verify this.

PAH testing took place from April through August, 1992 and involved the work of 4 researchers. Two researchers worked primarily at Deer Island and 2 worked primarily at Parsons Laboratory. The PAH sampling and testing was fraught with difficulties. The major difficulties were:

- 1) Developing appropriate sampling procedures;
- 2) Gaining access to Deer Island;
- 3) Analysis of such small concentrations of PAHs.

Sampling procedure:

Due to the small concentrations of PAHs generally found in wastewater (parts per trillion), a large volume (8 gallons per sample) had to be collected. Samples were collected in 8 one gallon glass bottles which had been prepared by rinsing with chromic acid. These 8 one gallon glass bottles were transported in a large cooler and made the trip from Parsons Laboratory to Deer Island and back to Parsons Laboratory either via the Boston Harbor Project Bus Transportation System or by MIT van. Gaining access to Deer Island for a private vehicle involved obtaining special permission and passes. Arrangements had to be made well in advance and any changes meant that new arrangements had to be coordinated.

Testing Procedure:

A successful testing procedure was developed based on a

scaling up of the jar test methodology. This batch test procedure used 10 gallon garbage cans as mixing vessels and a hand-held drill fitted with a paddle stirrer as a mixing device. An exact correlation between jar test mixing speeds and batch test mixing speeds was attempted and proved unworkable. Instead, 3 mixing speeds -- high, medium, and low -- were settled on as a means to obtain a rapid mix, a thorough stirring, and gentle flocculation. Appendix H gives the batch testing procedure.

Sampling Dates:

One or 2 samples were collected on 7 different days: April 21, June 12, June 19, July 6, July 13, July 27, and August 12. Results were obtained on 5 of these occasions: April 21, June 12, July 6, July 27, and August 12. The reasons results were not obtained on all occasions were:

- 1) Difficulty of analysis meant no results were possible for that sample;
- 2) Bottles broken in transport due to the rough construction roads on Deer Island;
- 3) Changed procedure recommended by lab personnel (leading to the discarding of that day's sample(s)).

Sample Analysis:

Preparing a PAH sample for analysis is an involved procedure entailing sample extraction using toluene, volume reduction from 8 gallon (30.4 liters) to less than 1 mL, and color chromatography. Sample analysis was performed using a Hewlett-Packard 5995 Gas Chromatograph/Mass Spectrometer. This instrument has a 0.25 micron 30m DB5 J&W scientific capillary column. The Parsons Laboratory PAH test procedure is given in Appendix H.

Results:

Results were obtained for 3 raw influent samples, 2 effluent samples, and 3 coagulation experiment samples (The complete PAH test results are provided in Appendix H). Unfortunately, of 8 intended chemical coagulation experiments which were planned for the summer test period:

- 1) 5 mg/l chitosan + 0.2 mg/l #2540
- 2) 20 mg/l FeCl₃ + 0.2 mg/l #2540
- 3) 20 mg/l FeCl₃ + 2 mg/l chitosan
- 4) 20 mg/l FeCl₃ + 2 mg/l *Moringa stenopetala*
- 5) 20 mg/l alum + 2 mg/l chitosan
- 6) 20 mg/l alum + 2 mg/l *Moringa stenopetala*
- 7) 5 mg/l chitosan + 2 mg/l *Moringa stenopetala*
- 8) 5 mg/l chitosan + 2 mg/l *Moringa oleifera*

results were only obtained for #2 and #3. The July 6th and the August 12th coagulation experiments used 20 mg/l ferric chloride + 0.2 mg/l #2540. The July 27th coagulation experiment used 20 mg/l ferric chloride + 2 mg/l chitosan. Thus comparisons of coagulation efficacy can be made only between these 2 chemical regimes.

Previous PAH testing at Deer Island had been performed by Batelle Ocean Science. On 3 consecutive days in November, 1991, Batelle Science had done PAH testing at the existing primary treatment facility. On each occasion, Batelle Science sampled and tested PAHs in the raw influent and in the effluent. The Batelle data, presented in Table 8, provides a baseline against which to evaluate the MIT Summer 1992 PAH test results:

TABLE 8
BATELLE OCEAN SCIENCE DEER ISLAND TREATMENT PLANT PAH TEST RESULTS⁴
NOVEMBER, 1991

	Average Influent (ng/l)	Average Effluent (ng/l)	% Removal
naphthalene	3171	1830	42
acenaphthylene	32	15	53
acenaphthene	ND	ND	ND
fluorene	641	218	66
phenanthrene	876	309	65
anthracene	63	27	56
methylphenanthrene + methylanthracene	355	102	71
fluoranthene	248	109	56
pyrene	278	110	60
methylfluoranthene methylpyrene			
benz[a]anthracene	87	35	59
chrysene	99	41	58
benzo[b]fluoranthene + benzo[k]fluoranthene	118	48	60
benzo[a]pyrene	55	20	64
benzo[e]pyrene	51	21	59
benzo[ghi]perylene	31	13	58
indeno[1,2,3-cd]pyrene	38	20	48
dibenz[a,h]anthracene	5	2	56

⁴ The complete data set of the Battelle Ocean Science data is given in Appendix H. The data was provided by Mike Conner of the Massachusetts Water Resources Authority.

Three raw influent samples and 2 effluent samples were collected and analyzed during the MIT PAH tests. The 3 influent tests, the first PAH tests performed during this summer test period, gave very low PAH concentrations. The influent results are not shown here but are given in Appendix H. The low concentrations of the 3 influent samples may, in fact, reflect very low influent PAH concentrations on those particular days. Alternatively, they may be "soft" results because the lab technicians were still gaining experience in this difficult analytic procedure. The PAH effluent results show higher concentrations than in the influent concentrations. Although this is possible, because the samples were obtained on different days, it is unlikely. We would expect to see effluent PAH concentrations lower than influent PAH concentrations. The effluent results are quite valuable, however, for comparing with the coagulation experiment results, especially because effluent samples were obtained on the same days as the coagulation experiments.

Table 9 presents the July 27th effluent and the July 27th coagulation experiment results in which the chemical regime was 20 mg/l ferric chloride and 2 mg/l chitosan. The second column in Table 9 is labeled "Average Effluent." This is the average of 2 gas chromatograph-mass spectrometer analyses performed on 1 effluent sample. The third column is labeled "Average FeCl₃ + Chitosan." This column is the average of 2 gas chromatograph-mass spectrometer analyses performed on 1 ferric chloride + chitosan coagulation experiment sample. The 4th column is labeled "% Improvement" and the 5th column is labeled "% removal." "% improvement" is the term we use in this report to indicate the increased efficiency relative to the wastewater effluent. "% removal" is the term we use to indicate the increased efficiency relative to the wastewater influent.

The "% improvement" column is calculated based on that day's PAH effluent sample. The % removal is computed based on the Batelle average influent concentration (Table 8).

TABLE 9
PAH RESULTS -- JULY 27, 1992

	Average Effluent (ng/l)	Average FeCl ₃ + chitosan (ng/l)	% Improve- ment	% Removal (w/ Batelle influent)
naphthalene	2386	311	87	90
acenaphthylene	90	26	70	17
acenaphthene	218	57	74	
fluorene	224	98	56	85
phenanthrene	312	171	45	81
anthracene	19	14	25	77
methylphenanthrene + methylantracene	199	107	46	70
fluoranthene	125	161	-29	35
pyrene	131	105	20	62
methylfluoranthene + methylpyrene	47	57	-21	
benz[a]anthracene	29	29	0	66
chrysene	51	36	29	64
benzo[b]fluoranthene + benso[k]fluoranthene	34	27	20	77
benzo[a]pyrene	33	33	0	40
benzo[e]pyrene	42	22	47	56
benzo[ghi]perylene +				
indeno[1,2,3-cd]pyrene		32		16
dibenz[a,h]anthracene				

An examination of this data shows us that the average PAH concentration for the ferric chloride plus chitosan coagulation experiment is generally lower than the average effluent concentration. This suggests that, in general, PAH concentrations were removed by the coagulation test.

Whereas the Batelle Ocean Science primary treatment PAH removal efficiency results shows a tighter range of % removals from 42% to 71%, the July 27th ferric chloride and chitosan data shows a % improvement all the way from -29% to 87%. Based on this, we cannot say that a chemical regime of ferric chloride and chitosan improves the removal of PAHs. Comparing the last 2 columns of Table 9 suggest the reasonable possibility that ferric chloride plus chitosan gives a % removal greater than the % improvement. This result, of course, hinges on whether we can accept the Batelle average influent data as representative. Until further tests are performed, we cannot say this with any certainty.

Table 10 gives the results of the August 12th effluent and coagulant tests. Again, the coagulant test results generally show lower PAH concentrations than the effluent results. The % improvement ranges from 18% to 92%. We suspect of the August 12th result that there has possibly been an oil spill. The concentrations of these samples are considerably higher than all previous MIT PAH tests. Also, the ratio of m/e 178 compounds to m/e 192 compounds and the ratio of m/e 202 compounds to m/e 216 compounds are low, supporting the idea of an oil spill (because during combustion, methyl groups are released). Because this is an unusual result relative to all earlier data, it is difficult to say whether the ferric chloride plus #2540 chemical regime performs better or worse than the ferric chloride plus chitosan regime. What can be said with some degree of assurance about both chemical coagulation experiments is that in general they show an improvement over the same day effluent results.

TABLE 10
PAH RESULTS -- AUGUST 12, 1992

	Effluent (ng/l)	FeCl3 + #2540 (ng/l)	% Improvement
naphthalene	4,116	1,738	58
acenaphthylene	ND		
acenaphthene	886	726	18
fluorene	3,810	2,087	45
phenanthrene	10,205	2,656	74
anthracene	261	188	28
methylphenanthrene + methylantracene	25,480	9,936	61
fluoranthene	3,719	300	92
pyrene	23,566	5,152	78
methylfluoranthene methylpyrene	94,536	15,232	84
benz[a]anthracene	1,287	ND	
chrysene	13,729	4,773	65
benzo[b]fluoranthene + benso[k]fluoranthene	1,977	366	81
benzo[a]pyrene	2,652	411	85
benzo[e]pyrene	6,408	1,969	69
benzo[ghi]perylene +			
indeno [1,2,3-cd] pyrene			
dibenz[a,h]anthracene			

PAH Summary:

Based on the data obtained to date, we can make the following summary statements:

- * Chemical coagulation using ferric chloride and a coagulant aid of either chitosan or #2540 generally gave PAH concentrations which were lower in the coagulation experiment than in the Deer Island effluent.
- * The relative efficiency of chitosan versus #2540 as competing coagulant aids/floculents could not be determined;
- * Chemical coagulation batch tests suggest that chemical addition may improve PAH removal in Deer Island wastewater relative to conventional primary treatment;
- * The efficacy of chitosan as a primary coagulant with or without the aid of other natural polymers could not be obtained due to the difficulties encountered with sample collection and laboratory analysis;
- * More tests are needed to determine the efficacy of metal salts, synthetic and/or natural polymers in removing PAHs from wastewater.

5. SLUDGE

Sludge production for chemical sludge using ferric chloride or natural polymers can be computed using the 3 equations given below. Assumed values for the different variables based on Deer Island flows and loads are also given. The rate of sludge production of the 2 chemical sludge alternatives is computed and compared:

Ferric Chloride Addition

$$S_{chem} = (TSS_{in} - TSS_{out}) + 0.66(FeCl3_{in}) + 1.42(P_{in} - P_{out}) \quad (\text{Eqn 1})$$

where:

S_{chem} = amount of dry sludge solids (mg/l)
 TSS_{in} = measured raw influent TSS concentration (mg/l)
 TSS_{out} = measured raw effluent TSS concentration (mg/l)
 $FeCl3_{in}$ = concentration of ferric chloride added (mg/l)
 P_{in} = measured influent phosphorus concentration
 P_{out} = measured effluent phosphorus concentration

The following assumptions are operative in determining sludge production for a ferric chloride sludge:

Assumptions

TSS_{in} = 167 mg/l
 TSS_{out} = 42 mg/l (75% removal)
 $FeCl3_{in}$ = 40 mg/l as ferric
 P_{in} = 6 mg/l
 P_{out} = 4.2 mg/l

Applying these assumptions to equation 1 gives:

$$\begin{aligned} S_{chem} &= (167\text{mg/l} - 42\text{mg/l}) + 0.66(40 \text{ mg/l}) + 1.42 (6\text{mg/l} - 4.2\text{mg/l}) \\ &= 154 \text{ mg/l} \end{aligned}$$

The annual rate of sludge production is determined by:

$$S'_{chem} = Q * S_{chem} * C * 365 \text{ days/yr} * 1\text{ton}/2000\text{lb} \quad (\text{Eqn 2})$$

where

S'_{chem} = rate of chemical sludge produced (dry tons/yr)
 Q = flow rate (mgd)
 C = conversion constant = 8.34 (lb/day)/(mgd)(mg/l)

Assuming a design flow at Deer Island of 480 mgd gives the

following sludge quantities:

$$\begin{aligned} S'_{\text{chem}} &= 480 \text{ mgd} * 154 \text{ mg/l} * 8.34 \text{ (lb/day)/(mgd) (mg/l)} \\ &\quad * 365 \text{ day/yr} * 1 \text{ ton/2000lb} \\ &= 112,510 \text{ tons/yr} \end{aligned}$$

Natural polymer sludge production can be determined by using a similar equation. There is no factor in front of the natural polymer variable because all the natural polymer will wind up in the sludge; none in the effluent.

Natural Polymer Addition

$$S_{\text{chem}} = (\text{TSS}_{\text{in}} - \text{TSS}_{\text{out}}) + (\text{Natural Polymer}_{\text{in}}) \quad (\text{Eqn 3})$$

where:

Natural Polymer_{in} = concentration of natural polymer added (mg/l)

It should be noted also that the natural polymer sludge equation does not have a term for phosphorus removal. Testing in Gloucester, MA showed that natural polymers do not have the advantage metal salts do of increasing phosphorus removal (Murcott and Harleman, 1992).

The following set of assumptions apply for a natural polymer sludge at Deer Island:

Assumptions

$$\text{TSS}_{\text{in}} = 167 \text{ mg/l}$$

$$\text{TSS}_{\text{out}} = 50 \text{ mg/l (70\% removal)}$$

$$\text{Natural Polymer}_{\text{in}} = 5 \text{ mg/l chitosan} + 1 \text{ mg/l Moringa Stenopetala}$$

The amount of sludge solids produced with natural polymers is:

$$\begin{aligned} S_{\text{chem}} &= (167 \text{ mg/l} - 50 \text{ mg/l}) + 6 \text{ mg/l} \\ &= 123 \text{ mg/l} \end{aligned}$$

The rate of sludge production with natural polymers is:

$$\begin{aligned} S'_{\text{chem}} &= 480 \text{ mgd} * 123 \text{ mg/l} * 8.34 \text{ (lb/day)/(mgd) (mg/l)} \\ &\quad * 365 \text{ day/yr} * 1 \text{ ton/2000lb} \\ &= 89,862 \text{ tons/yr} \end{aligned}$$

Table 11 summarizes these results:

TABLE 11
ESTIMATED ANNUAL SLUDGE PRODUCTION SUMMARY

Ferric Chloride Sludge	113,000 dry tons/yr (1.24 lb/lb TSS removed)
Natural Polymer Sludge	90,000 dry tons/yr (1.05 lb/lb TSS removed)

The annual rate of ferric chloride sludge production is 26% greater than that of natural polymer sludge. Although the use of ferric chloride provides a higher removal efficiency (in this example, 75% as opposed to 70% TSS removal), the larger quantity of ferric chloride required leads to a greater quantity of sludge.

6. ECONOMIC ANALYSIS

The purpose of this section of the report is to consider the economic viability of using chitosan in wastewater treatment. This will be accomplished by comparing the operation and maintenance (O&M) costs associated with 2 alternate chemical options in each of 4 cases. The principal components of the overall O&M cost which may be affected by the choice of chemicals are the cost of the liquid treatment process and the cost of sludge handling and disposal. The effects of either chemical option on capital costs are insignificant and are therefore not included in this discussion.

Two chemical options are under consideration, both of which are applied in the primary stage of a treatment.

- * Option 1 consists of the use ferric chloride and an anionic polymer to upgrade conventional primary treatment to chemically enhanced primary treatment.
- * Option 2 consists of the use of chitosan and *Moringa stenopetala* to upgrade conventional primary treatment to chemically enhanced primary treatment.

We will consider 4 cases, as follows:

CASE 1: MUNICIPAL WASTEWATER

- * Current market price for both chemical options;
- * Land application of both types of chemical sludge.

CASE 2: MUNICIPAL WASTEWATER

- * Current market price of ferric chloride;
- * Estimated "bulk" price of chitosan;
- * Land application of both types of chemical sludge.

CASE 3: MUNICIPAL WASTEWATER

- * Current market price of ferric chloride;
- * Estimated "bulk" price of chitosan;
- * Landfilling of ferric chloride sludge;
- * Land application of chitosan sludge.

CASE 4: FOOD PROCESSING INDUSTRIAL WASTEWATER

- * Current market price of ferric chloride;
- * Estimated "bulk" price of chitosan;
- * Landfilling of ferric chloride sludge;
- * Chitosan sludge as a reusable animal feed product.

Case 4 expands the terms of the inquiry to consider chemical treatment of an industrial food processing wastewater. All other cases consider municipal wastewater.

In carrying out the economic analysis, we have made size and cost assumptions based on values derived from the Boston Harbor Cleanup Project. These assumptions and costs were chosen not because any of the 4 cases applies to new facilities under construction at Deer Island and at Quincy, but simply because the Boston Harbor Cleanup Project is a good and comprehensive source of engineering and economic data. These assumptions are simply meant to provide a framework for the discussion.

What we intend now is to work through one case, Case 2, providing the sources for the cost estimates as we go through the example. After the methodology is clear to the reader, we will comment on the other 3 cases. Case 2 will elucidate Case 1 and Case 3. Case 4 will involve a somewhat separate discussion.

Liquid Process Operation & Maintenance Costs:

The annual O&M costs of the liquid process as impacted by the use of chemicals are based on the following assumptions⁵:

- * Maintenance costs are 2% of equipment capital cost including pumps, piping systems, instrumentation & electrical;
- * Cost of electricity is \$0.063/kw-hr;
- * 24 hr/day operation for metering pumps;
- * 8 hr/day operation for transfer pumps and day tanks;
- * 4 month/yr operation for chemical storage and day tank heaters;
- * Chemical Costs:

Ferric Chloride	\$0.10/dry lb
Anionic Polymer	\$2.00/dry
Chitosan	\$3.50/dry lb ⁶
<i>Moringa stenopetala</i>	\$1.00/dry lb ⁷

⁵ The format for the evaluation of the liquid process O&M costs follows the Metcalf & Eddy "Advanced Primary Treatment Study" presented to the Mass. Water Resources Authority by Daniel O'Brien, Senior Design Manager, Metcalf and Eddy, in July, 1990.

⁶ This cost estimate has been provided by Lee Johnson, President of Vanson Chemicals, Inc., manufacturer of chitosan, based on the assumption of the purchase of a large quantity of chitosan.

⁷ This is a rough estimate, based on the cost of the *Moringa stenopetala* purchased from Banana Tree, Inc., an exotic seed company in Easton, Pennsylvania.

* Chemical Dosage Rates:		
	Ferric Chloride	40 mg/l
	Anionic Polymer	0.2 mg/l
	Chitosan	5 mg/l
	<i>Moringa Stenopetala</i>	1 mg/l
* TSS Removal		
	Option 1 Chemical Regime	75%
	Option 2 Chemical Regime	70%
* BOD Removal		
	Option 1 Chemical Regime	50%
	Option 2 Chemical Regime	45%

Table 12 summarizes these O&M costs:

TABLE 12
LIQUID PROCESS OPERATION AND MAINTENANCE COSTS (\$)
***** OPTION 1 *** *** OPTION 2 *****

	Ferric Chloride	Anionic Polymer	Chitosan	<i>Moringa Stenopetala</i>
Operation	144,700	141,500	144,700	141,500
Maintenance	13,200	2,000	13,200	2,000
Chemicals	5,844,700	584,500	25,570,400	1,461,200
Subtotal	6,002,600	728,000	25,728,300	1,604,700

Based on the values given in Table 11, the total liquid process O&M costs for the 2 chemical options are presented in Table 13:

TABLE 13
ANNUAL OPERATION AND MAINTENANCE COSTS FOR 2 CHEMICAL OPTIONS

Option 1: Ferric Chloride + Anion	\$6,730,600
Option 2: Chitosan + <i>Moringa Stenopetala</i>	\$27,333,000

Sludge Handling and Disposal Operation and Maintenance Costs:

For Case 2, we assume that the method of sludge disposal for both chemical sludges is land application. When chemical coagulants are added to the primary stage of the liquid treatment process, the bulk of those chemicals settle out into the wastewater sludge. Instead of generating a conventional primary sludge, as would be the case were no chemicals added, one generates a chemical sludge. The quality of either a primary or a chemical sludge will be impacted first and foremost by the

quality of the source. If the source has high concentrations of metals and/or toxic chemicals, then the sludge will probably be of a low quality and this will likely have an impact on sludge handling and disposal costs. In addition, the quality of a chemical sludge is affected by the chemicals added. A chemical sludge can have advantages or disadvantages depending on the type and grade of chemical coagulants used. These advantages and disadvantages will also impact sludge handling and disposal costs. For example, the addition of lime or iron salts in wastewater treatment can have a beneficial effect if sludge is applied to acidic or iron-poor soils. A substance such as chitosan, which has been shown to stimulate plant growth and which has also been approved by the industry group, the American Association of Feed Control Officials (AAFCO), could likewise contribute to the generation of a beneficial sludge. It is for reasons like these that the selection of land application for both types of sludge, as has been done in Case 2, could be valid.

Sludge quantity, as we have seen in Section 5 of this report, varies depending on the choice of chemicals. Sludge quantity for Option 1 and Option 2 are:

TABLE 14
ANNUAL SLUDGE QUANTITY

Option 1: Ferric Chloride Sludge	113,000 dry tons/yr
Option 2: Natural Polymer Sludge	90,000 dry tons/yr

Two sets of costs for the various sludge handling and disposal methods are provided below. The first set represents internal estimates used by the Massachusetts Water Resources Authority (MWRA) for evaluation of the various alternatives (Schiemann, C. 1992; Outwater, A. 1989). The MWRA costs are presented in Table 15:

TABLE 15
COST OF SLUDGE HANDLING AND DISPOSAL
DEER ISLAND WASTEWATER SLUDGE
(\$/dry ton of sludge)

	Processing	Transportation	Disposal	Total
Land Application	0	150	0	150
Compost	375	100	-10	465
Pellets	450	50	-50	450
Landfill	0	100	300	400
Chemfix	200	100	0	300
Incineration	300	100	0	400
Ocean Disposal	0	50	0	50

(Schiemann, C., 1992; Outwater, A. 1989)

The second set of costs is from the National Research Council "Committee on Wastewater Management in Coastal Urban Areas." These costs are expressed as a range, depending on the solids content and the quantity of sludge disposed. Processing, transportation, and disposal have all been factored into these costs. The NRC costs have been rounded off and are presented in Table 16:

TABLE 16
COST OF SLUDGE HANDLING AND DISPOSAL
(\$/dry ton of sludge)

Land Application	\$150 - \$200
Compost	\$600 - \$1200
Landfill	\$200 - \$300
Incineration	\$350 - \$650

(NRC, 1993)

Comparing these 2 sets of costs, the MWRA costs of land application and incineration appear to be confirmed by the NRC costs. The MWRA costs for the landfill alternative are high relative to the NRC costs, but this is reasonable, as landfill space is at a premium in Massachusetts. Finally, the MWRA costs for the compost option appear low. The 2 sets of costs have been provided for comparative purposes. For this analysis, we will use the MWRA costs as the basis for the next set of cost calculations.

Next we compute the sludge handling and disposal cost for the land application option. Table 17 shows that calculation:

TABLE 17
SLUDGE HANDLING AND DISPOSAL OPERATION & MAINTENANCE COSTS
FOR 2 CHEMICAL TREATMENT OPTIONS

	Quantity (dry tons /yr)	Sludge Method Cost (\$/dry ton)	Total Sludge O&M Cost (\$million)
Option 1: FeCl ₃ + Anionic Sludge	113,000	\$150 (land application)	\$17.0M
Option 2: Natural Polymer Sludge	90,000	\$150 (land application)	\$13.5M

Total O&M costs for both the liquid and the sludge processes under the Case 2 assumptions are tallied in Table 18:

TABLE 18
CASE 2 -- TOTAL OPERATION AND MAINTENANCE COST SUMMARY

	Total Liquid Process O&M (\$ million)	Total Sludge Process O&M (\$ million)	Total O&M (\$ million)
Option 1: FeCl ₃ + Anionic Sludge	\$6.7M	\$17.0M	\$23.7M
Option 2: Natural Polymer Sludge	\$27.3	\$13.5M	\$40.5M

The result of this analysis under Case 2 assumptions is that the total O&M cost for Option 1 is 41% less expensive than the total O&M cost for Option 2. This is mainly due to the high cost of chitosan, even at the "bulk" rate assumed under Case 2. Given the selection of the same sludge handling and disposal option, the O&M sludge cost difference is simply due to the effect of the different quantities of sludge.

Using the same methodology and set of assumptions, Table 19 has been developed to show the costs involved in all 4 cases.

TABLE 19
**4 CASES SHOWING A VARIETY OF CHEMICAL,
SLUDGE DISPOSAL AND COST OPTIONS**

Chemical	Cost	Liquid Process O&M Cost	Amount of Sludge	Sludge Disposal Method	Sludge Disposal Cost	Reusable Product	Total Sludge O&M Cost	Total Sludge Benefit	Total O&M Cost	Total O&M Benefit
	\$/lb	\$ in millions	dry tons/yr		\$/dry tons	\$/dry ton	\$ in millions	\$ in millions	\$ in millions	\$ in millions
CASE 1										
ferrie chloride	\$0.10	\$6.7M	113,000	land apply	\$150		\$17.0M		\$23.7M	
chitosan + MS	\$6.00	\$44.0M	90,000	land apply	\$150		\$13.5M		\$57.5M	
CASE 2										
ferrie chloride	\$0.10	\$6.7M	113,000	land apply	\$150		\$17.0M		\$23.7M	
chitosan + MS	\$3.50	\$27.3M	90,000	land apply	\$150		\$13.5M		\$40.8M	
CASE 3										
ferrie chloride	\$0.10	\$6.7M	113,000	landfill	\$400		\$45.2M		\$51.9M	
chitosan + MS	\$3.50	\$27.3M	90,000	land apply	\$150		\$13.5M		\$40.8M	
CASE 4										
ferrie chloride	\$0.10	\$6.7M	113,000	landfill	\$400		\$45.2M		\$51.9M	
chitosan + MS	\$3.50	\$27.3M	90,000	reusable product	\$0	\$500	\$0	\$45.0M	\$0	\$17.7M

Case 1 assumes the current market price of chitosan. Option 2 of Case 1 is out of the question for municipal wastewater treatment at this chitosan cost. Case 3 makes the assumption that the ferric chloride sludge is landfilled and the chitosan sludge is land applied. This might be a reasonable assumption for a situation such as in New England where the soils are already iron-rich. Also, metals salt sludges contain large amounts of aluminum and iron hydroxides, which are strong adsorbents of inorganic phosphorus. If such sludges are land-applied, extra fertilizer would be needed in order to obtain the desired crop yields (Elliott, H. et.al., 1990). This is a management and cost issue that might lead to a decision to landfill rather than land apply a metal salt sludge.

Case 4 departs most radically from the other 3 cases in its assumption of a industrial food processing wastewater. This case is included to show the benefit of generating a reusable product from the sludge in order to create a profit. The assumptions used to arrive at the costs are identical as those for the other cases.⁸

This economic analysis is intended as a "first cut" based on the best available information at the time of writing. It is also intended to be a framework within which to play with the variables, particularly the variables of natural polymer costs, sludge handling and disposal options, and reusable product prices as new information becomes available. That new information could include, but would not be limited to, the possibility of decreasing costs for natural polymers as a market for these products is developed and the likely impact of the new federal Environmental Protection Agency Sludge Regulations, due out in November, 1992, applicable to all municipal wastewater sludges. It is expected that these new regulations will set numerical limits for chemical characteristics of sludges and on the basis of these limits will establish 3 types of sludge: Type A, Type B, and Type C. While Type A sludge will be suitable for various kinds of land application, Type C sludge will not. These new regulations are expected to put a big emphasis on the creation of a reusable sludge. They will have a tremendous impact on sludge generation, characteristics, handling and disposal.

This analysis has not included any consideration of non-quantifiable economic benefits derived from the use of nontoxic, biodegradable, renewable chemical resources in wastewater treatment processes. It is nevertheless apparent that in the long run, treatment process chemicals that have these favorable characteristics will be preferred to those that lack the same.

⁸ The price of "soluble protein concentrate," the product derived from using chitosan in industrial food processing wastewater, has been conservatively estimated at \$0.25/dry lb, or \$500 dry/ton by S. Goldhor.

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Summary:

The following points summarize the economic analysis:

- * Chitosan is too expensive at the current market price and perhaps even at the estimated "bulk" quantity price to be viable at this time as a treatment chemical for municipal wastewater applications;

- * Chitosan and other chemical treatment processes that contribute to the generation of beneficial sludges that can be land applied will, at the current costs of sludge disposal, have an economic advantage over treatment processes that do not;

- * Chitosan and other natural polymers that can be used in generating a reusable animal feed product, such as soluble protein concentrate, from the application of the chemicals in an industrial food processing wastewater, is cost-effective.

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Figure 1
Chitosan as a Primary Coagulant
COD % Removal vs. Chitosan Concentration
Deer Island, Massachusetts

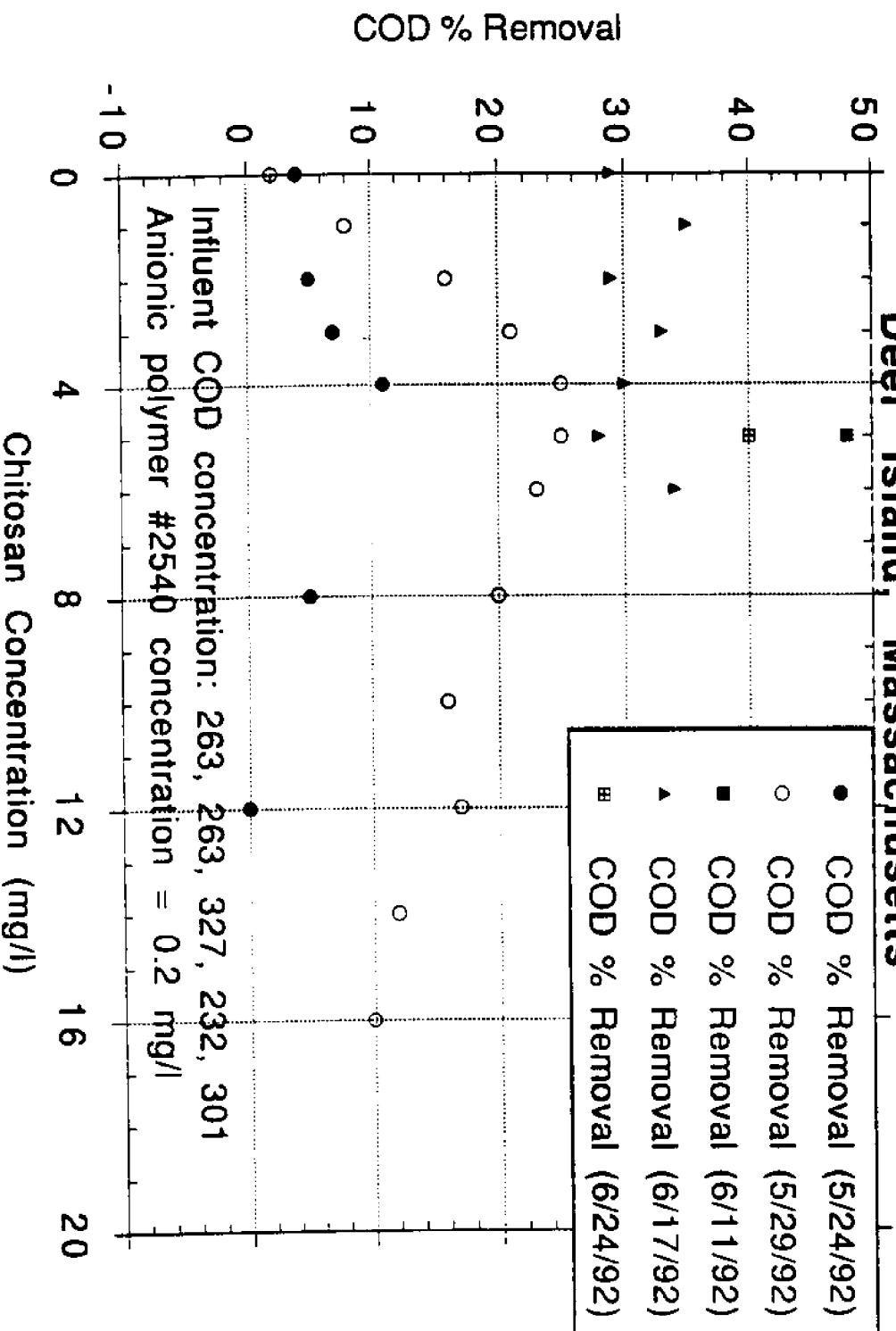


Figure 2
Chitosan as a Primary Coagulant
COD % Removal for Various Anionic Polymers
at Deer Island 6/11/92

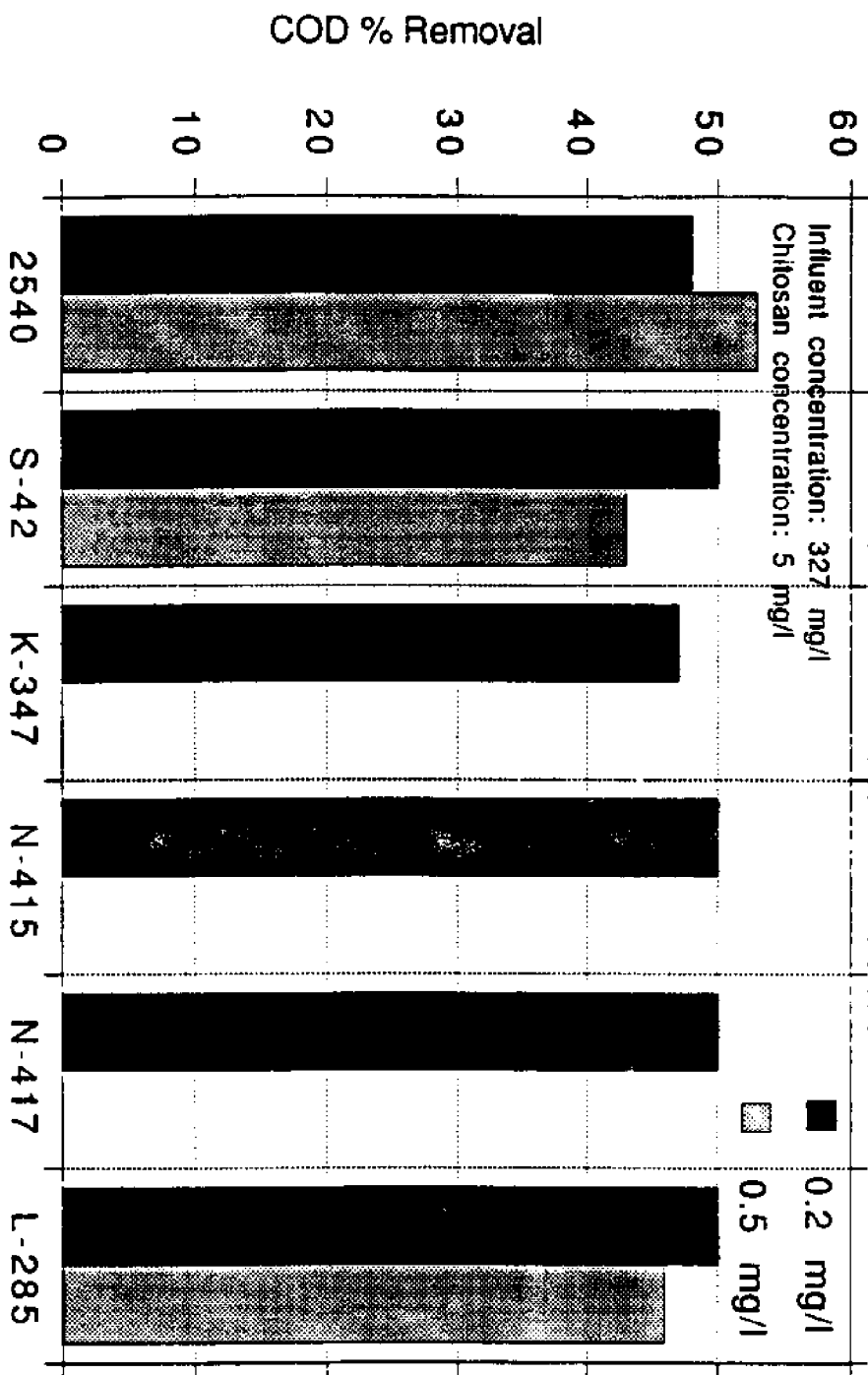


Figure 3

**Effect of Influent Concentration on COD % Removal
Chitosan as a Primary Coagulant
Deer Island, Massachusetts**

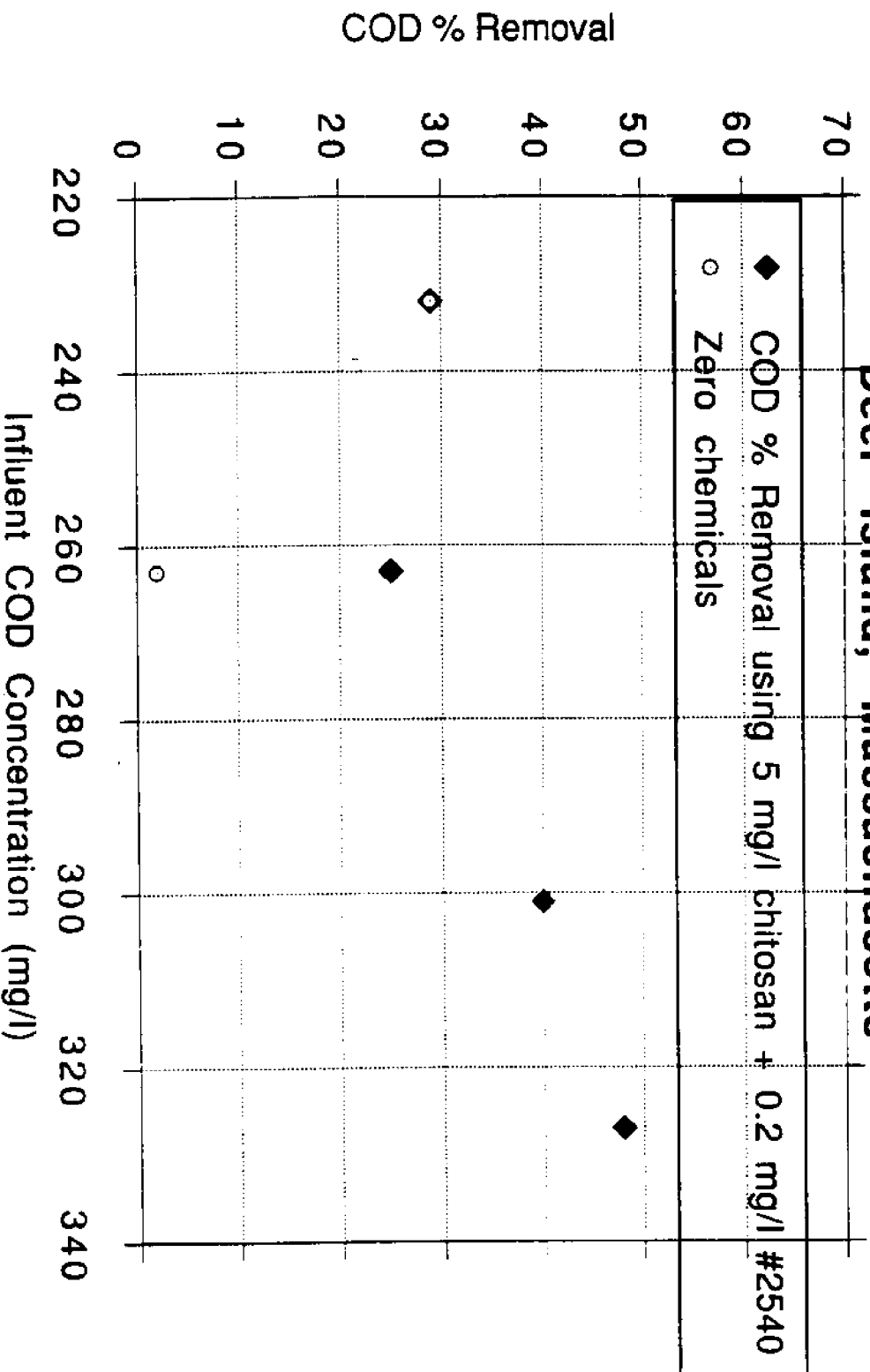


Figure 4
Effect of Temperature on COD % Removal
Chitosan as a Primary Coagulant
Deer Island, Massachusetts

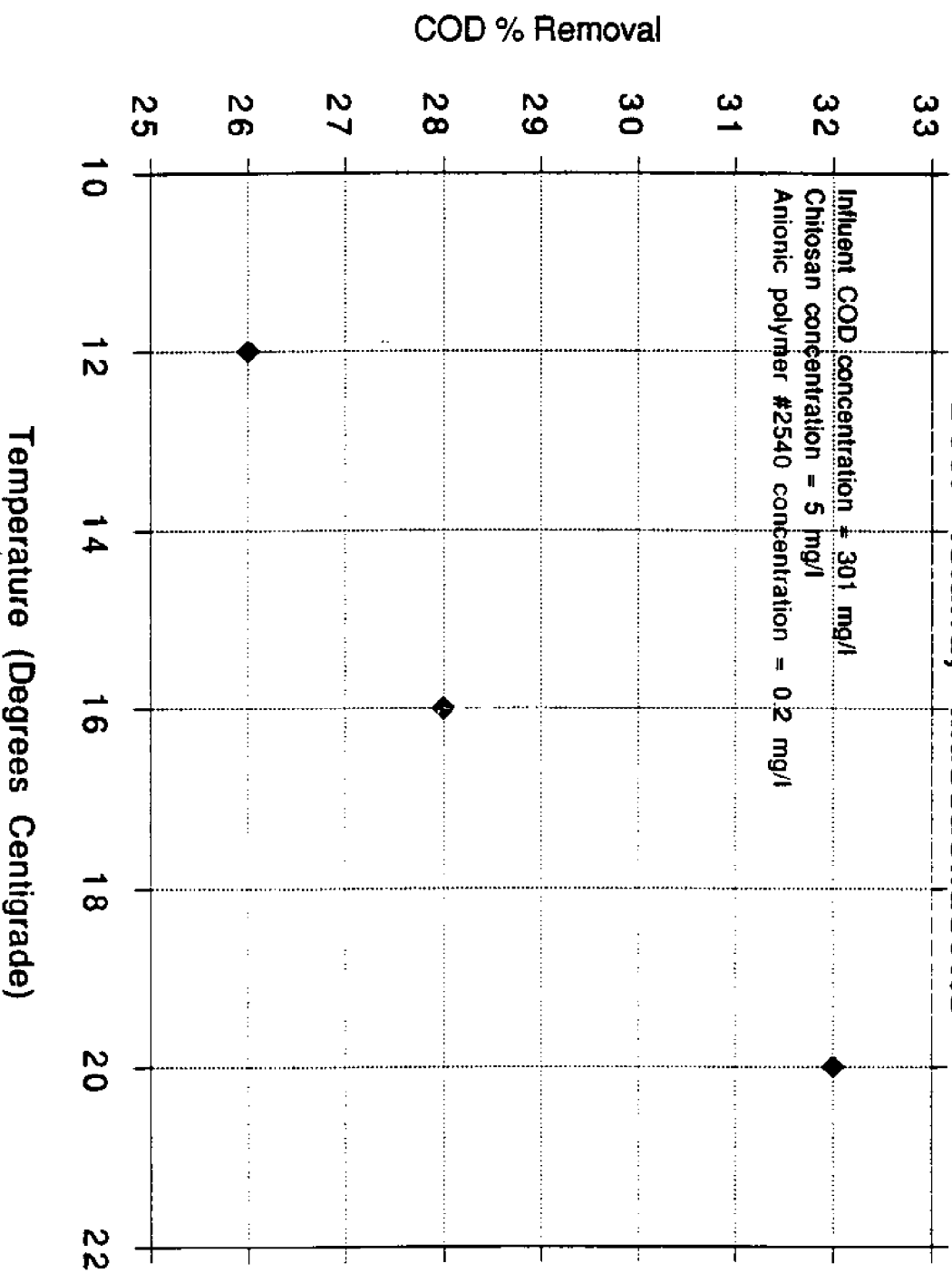


Figure 5
Effect of Mixing Speed on COD % Removal
Chitosan as a Primary Coagulant
Deer Island, Massachusetts

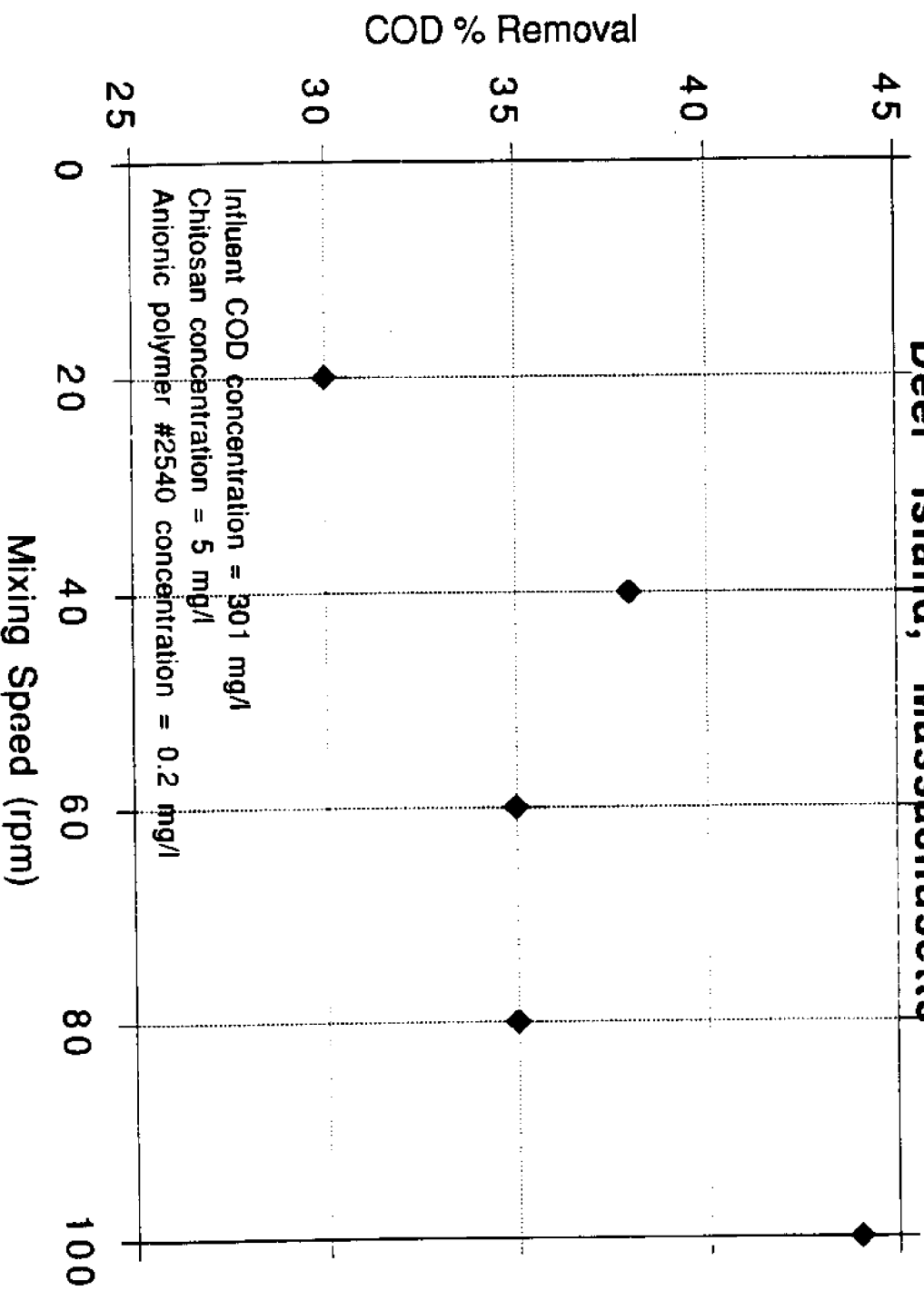


Figure 6
Effect of Mixing Time on COD % Removal
Chitosan as a Primary Coagulant
Deer Island, Massachusetts

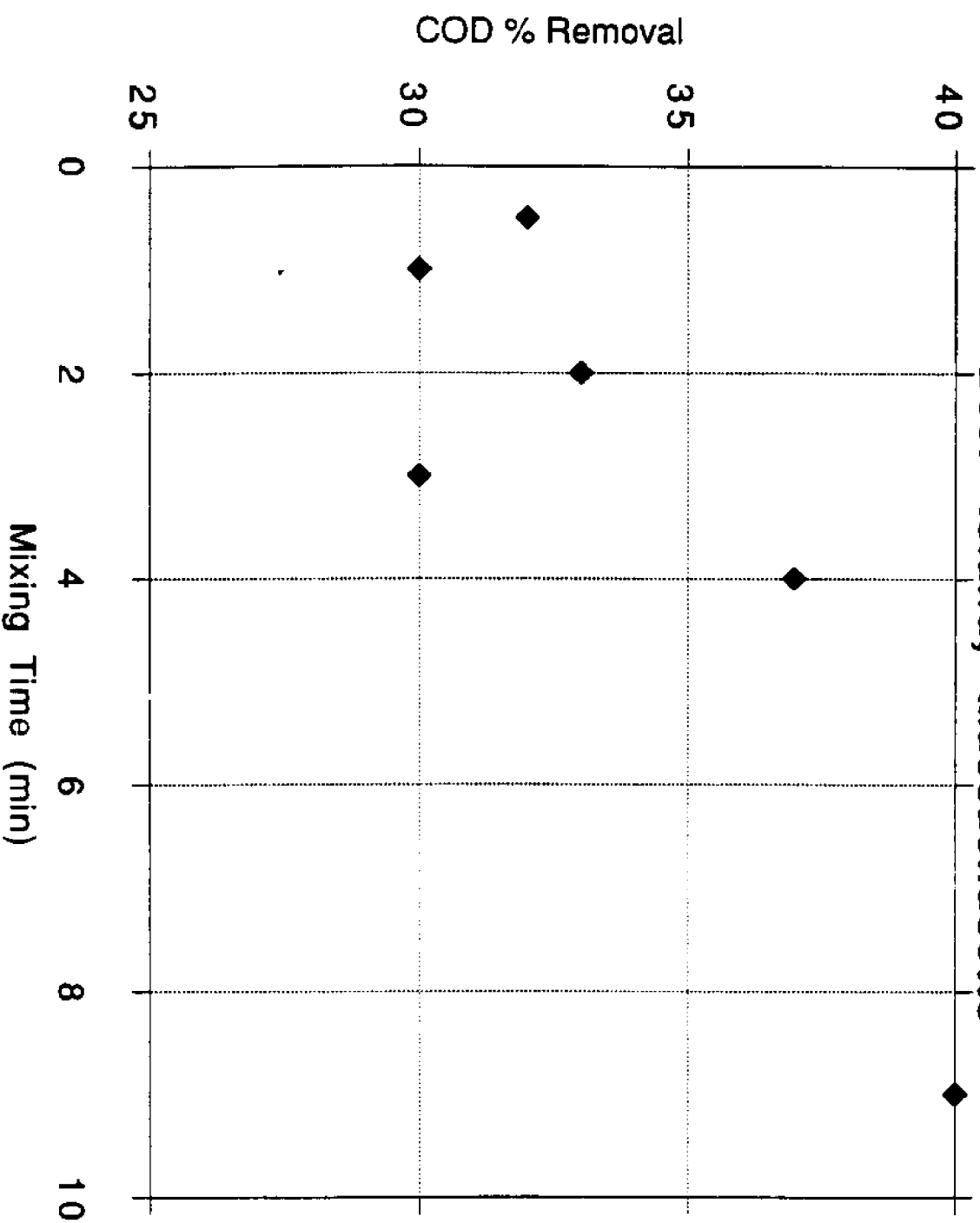


Figure 7
Effect of Mixing and Settling Time on COD % Removal
Chitosan as a Primary Coagulant
Deer Island, Massachusetts

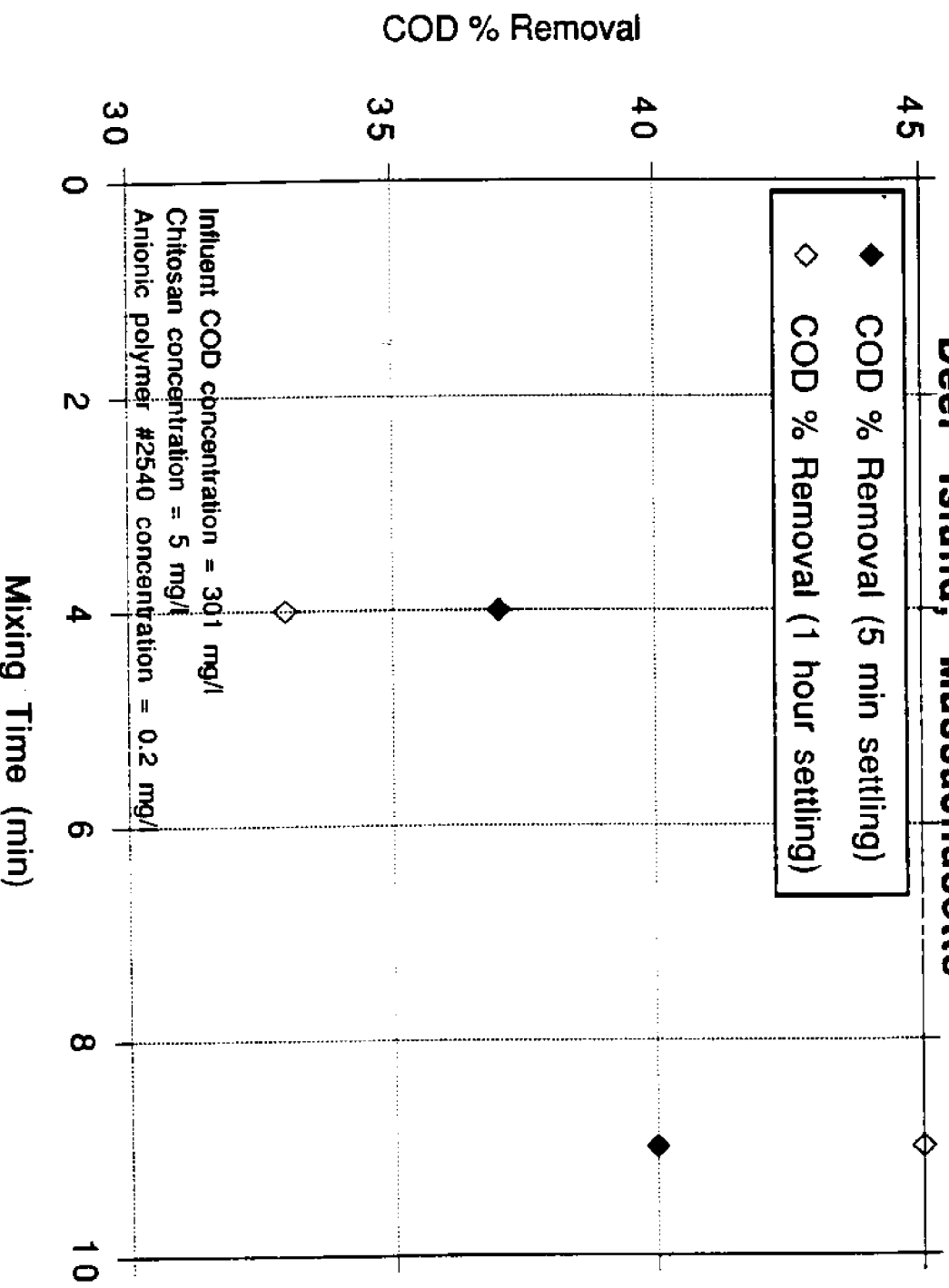
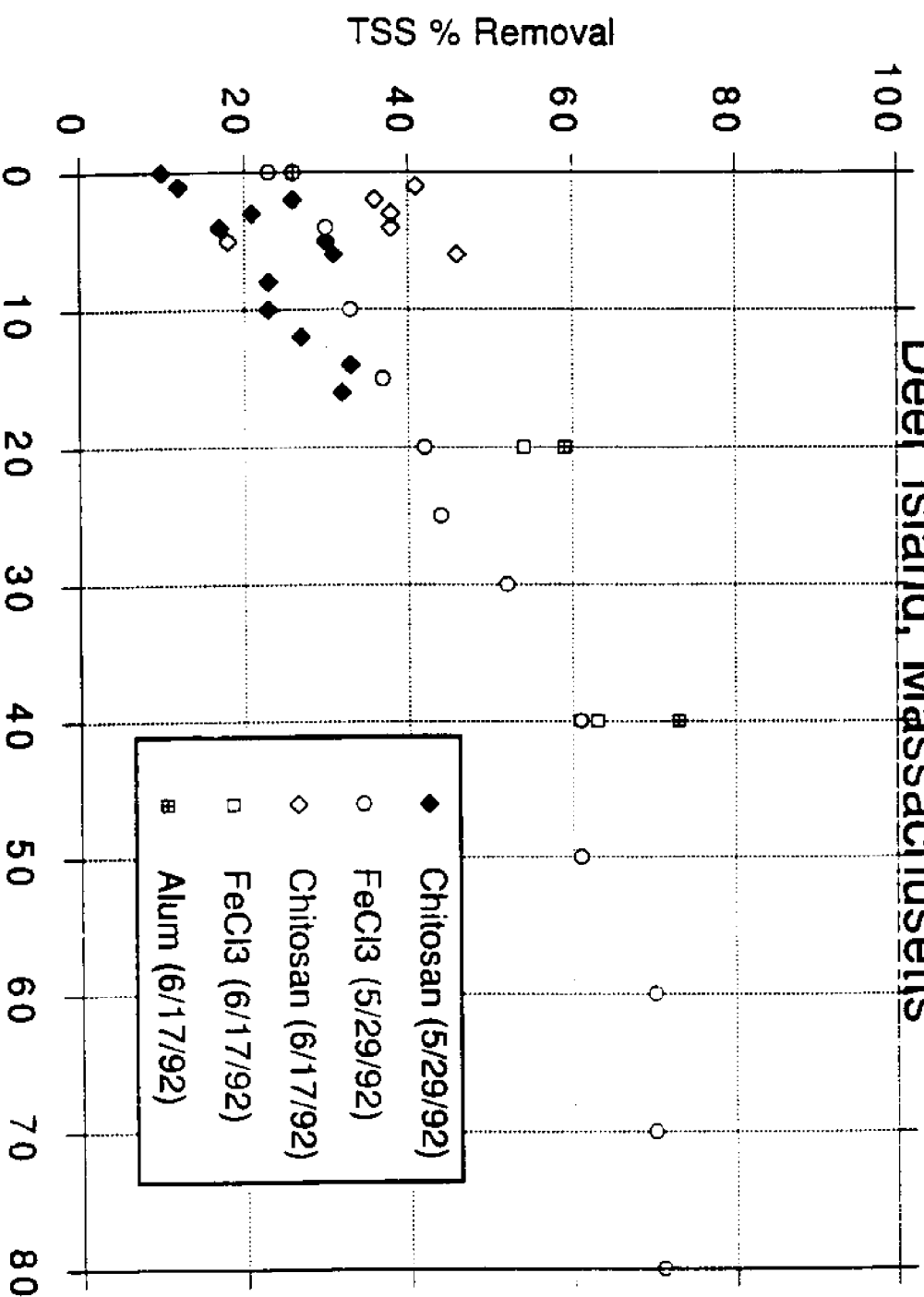
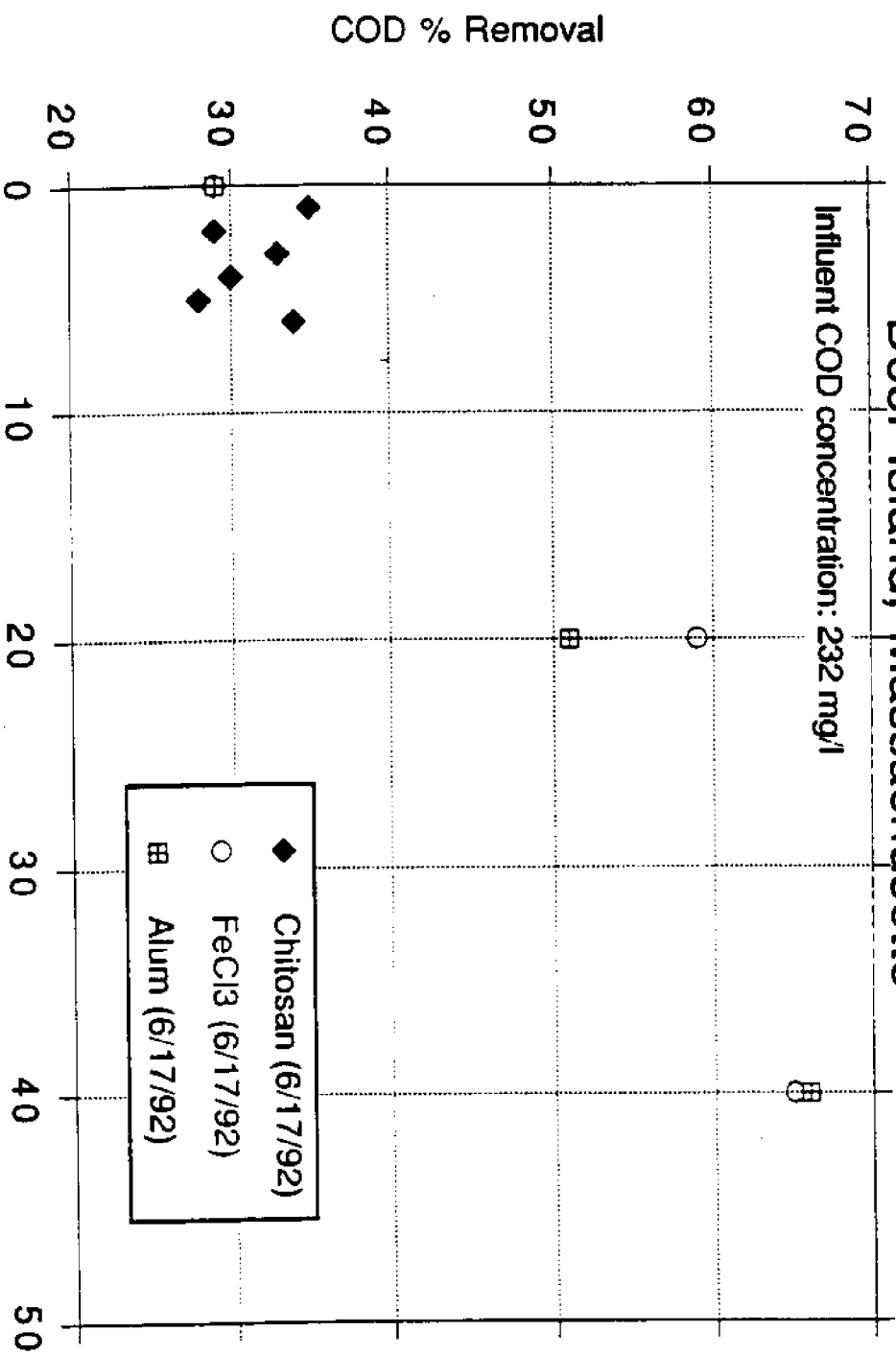


Figure 8
Comparison of Chitosan vs. Metal Salts as Primary Coagulants
TSS % Removal vs. Coagulant Concentration
Deer Island, Massachusetts



Note: All chemical regimes used 0.2 mg/l #2540 as a flocculent

Figure 9
Comparison of Chitosan & Metal Salts as Primary Coagulants
COD % Removal vs. Coagulant Concentration
Deer Island, Massachusetts



Note: All chemical regimes used 0.2 mg/l #2540 as a flocculent

Figure 10
Comparison of Chitosan & Ferric Chloride in Demineralized Water
COD Concentration vs. Coagulant Concentration
Deer Island, Massachusetts

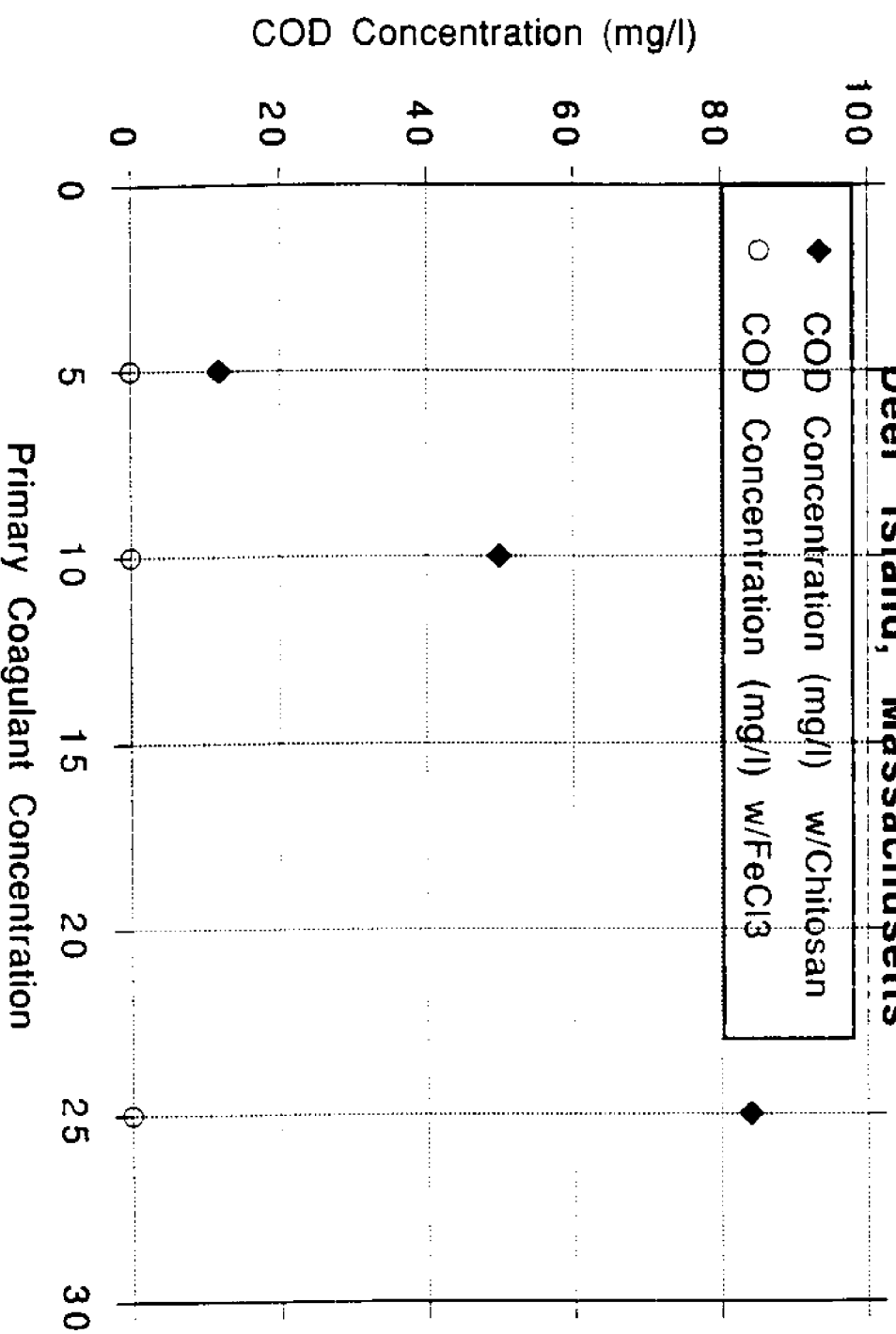


Figure 11

**Chitosan as a Primary Coagulant + Moringa Stenopetala
as a Coagulant Aid, with and without a Flocculent
COD % Removal vs. Moringa Concentration**

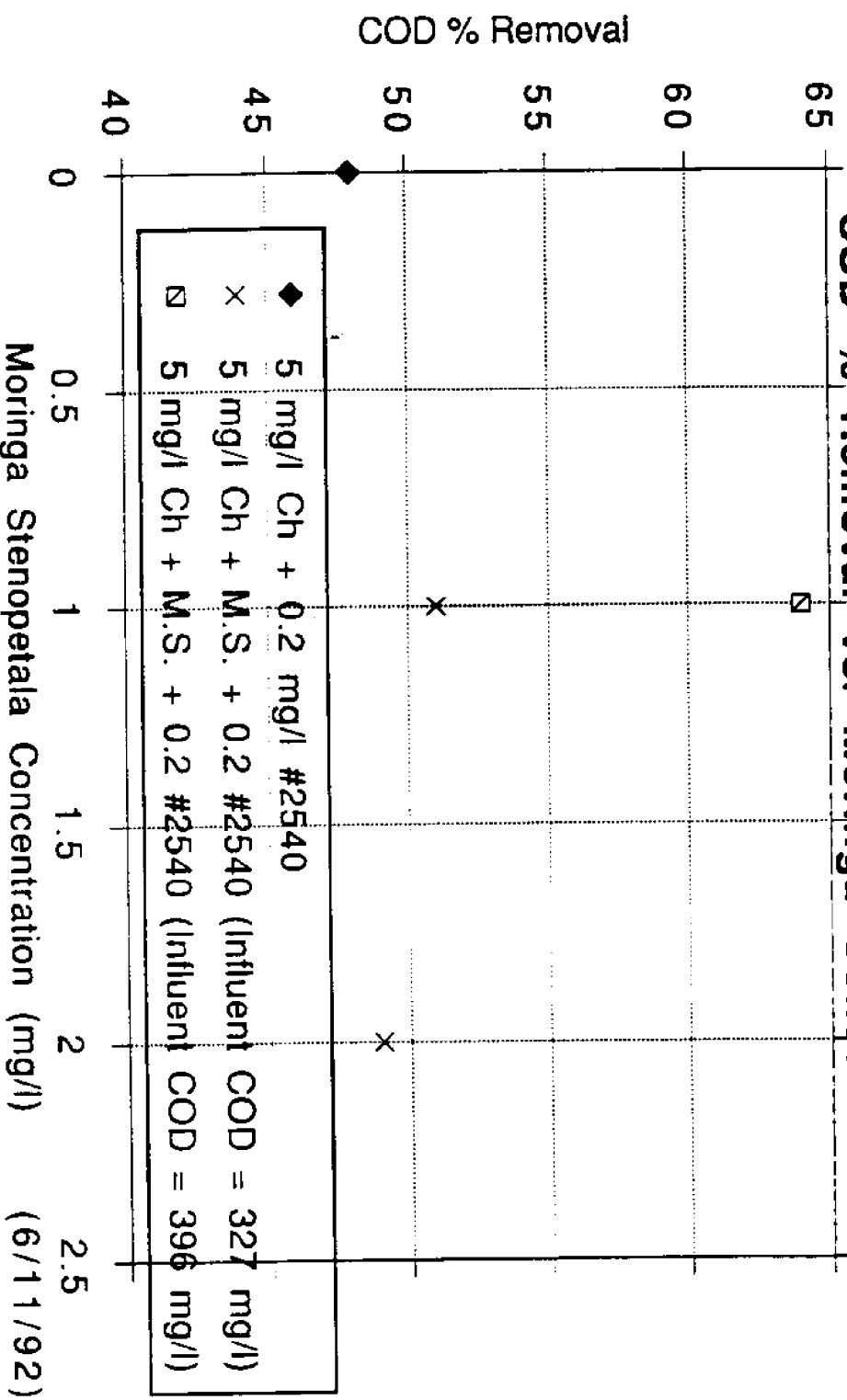


Figure 12
Chitosan as a Primary Coagulant + Moringa Stenopetala
as a Coagulant Aid with Various Flocculents
COD % Removal

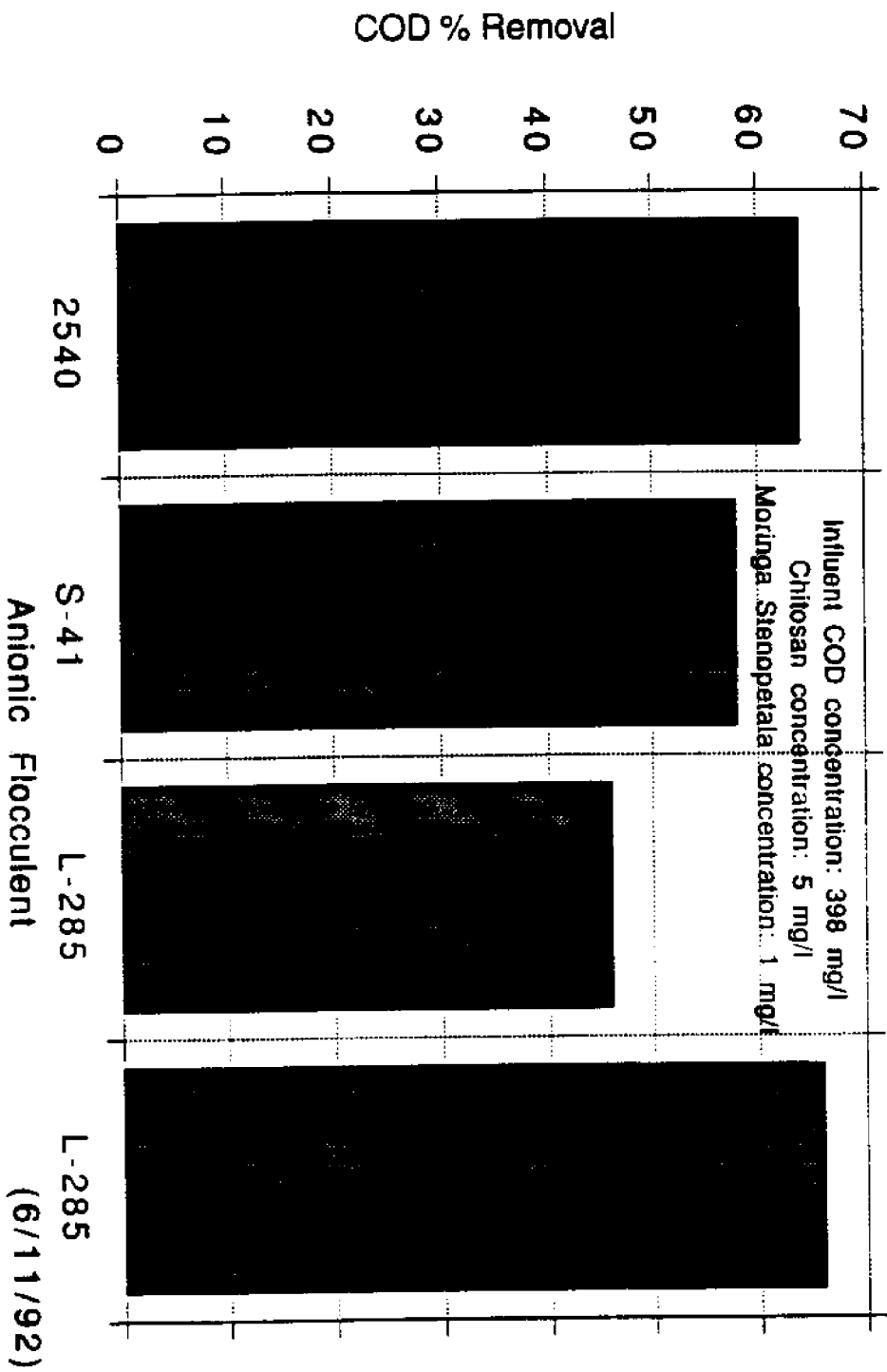


Figure 13
Ferric Chloride + Chitosan as a Coagulant Aid
with and without a Flocculent

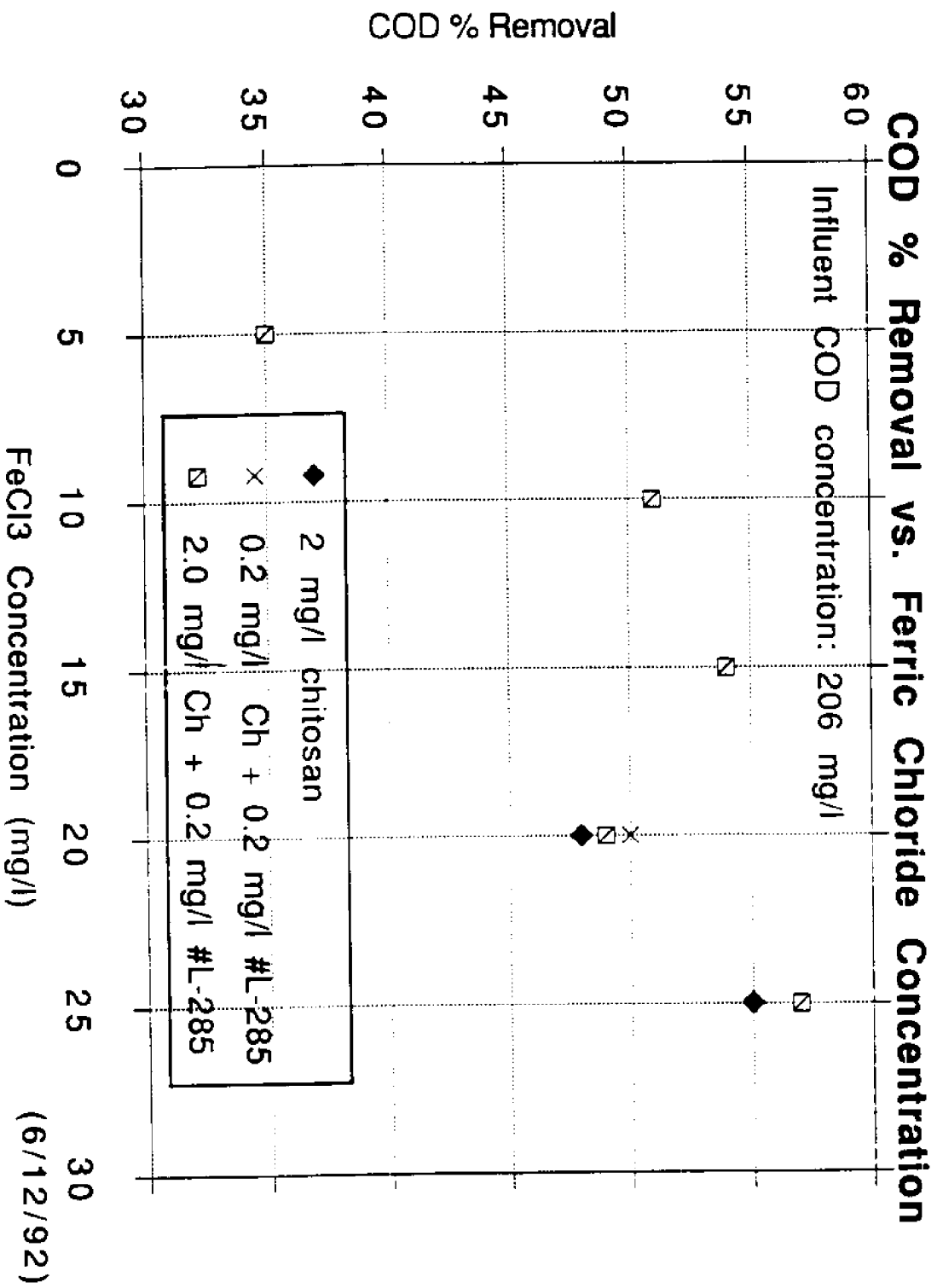


Figure 14

**Ferric Chloride + Chitosan as a Coagulant Aid
with and without a Flocculent**

COD % Removal vs. FeCl_3 Concentration

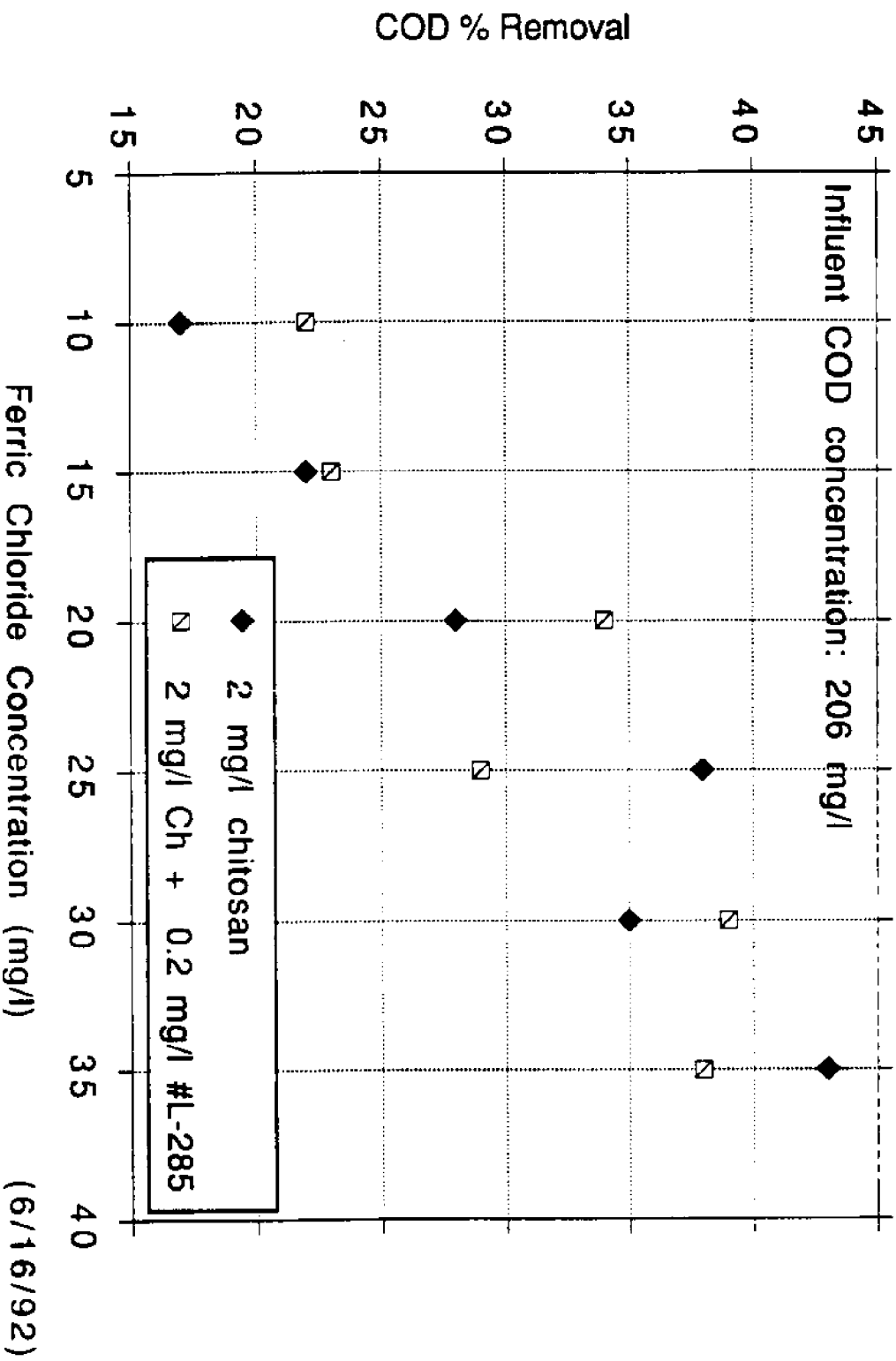
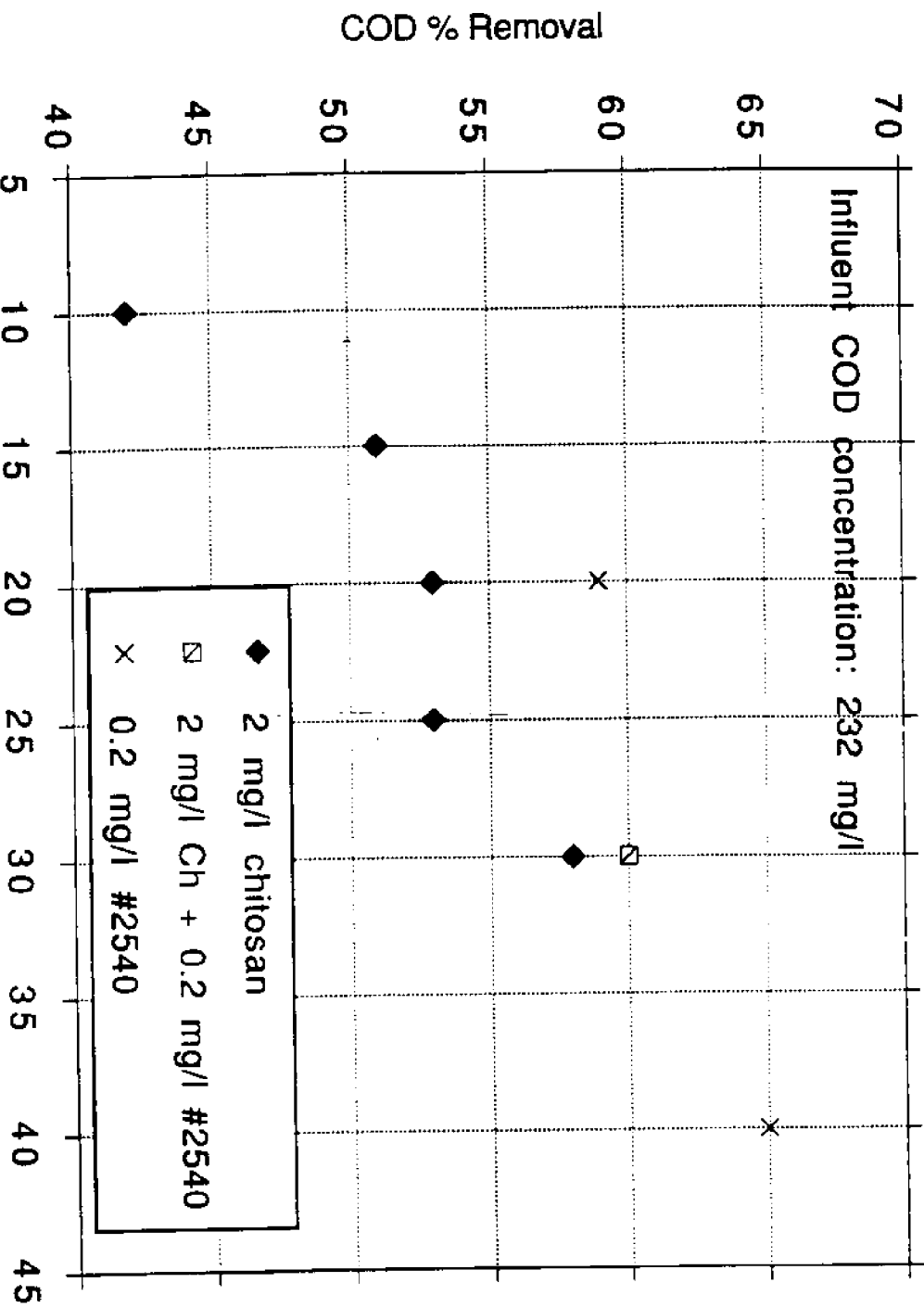


Figure 15

**Ferric Chloride with and without Chitosan
with and without a Flocculent**

COD % Removal vs. Ferric Chloride Concentration,



Ferric Chloride Concentration (mg/l)

(6/17/92)

Figure 16
Comparison of Chitosan vs. Various Synthetic Cationic Coagulant A1D5
in Removal of % COD

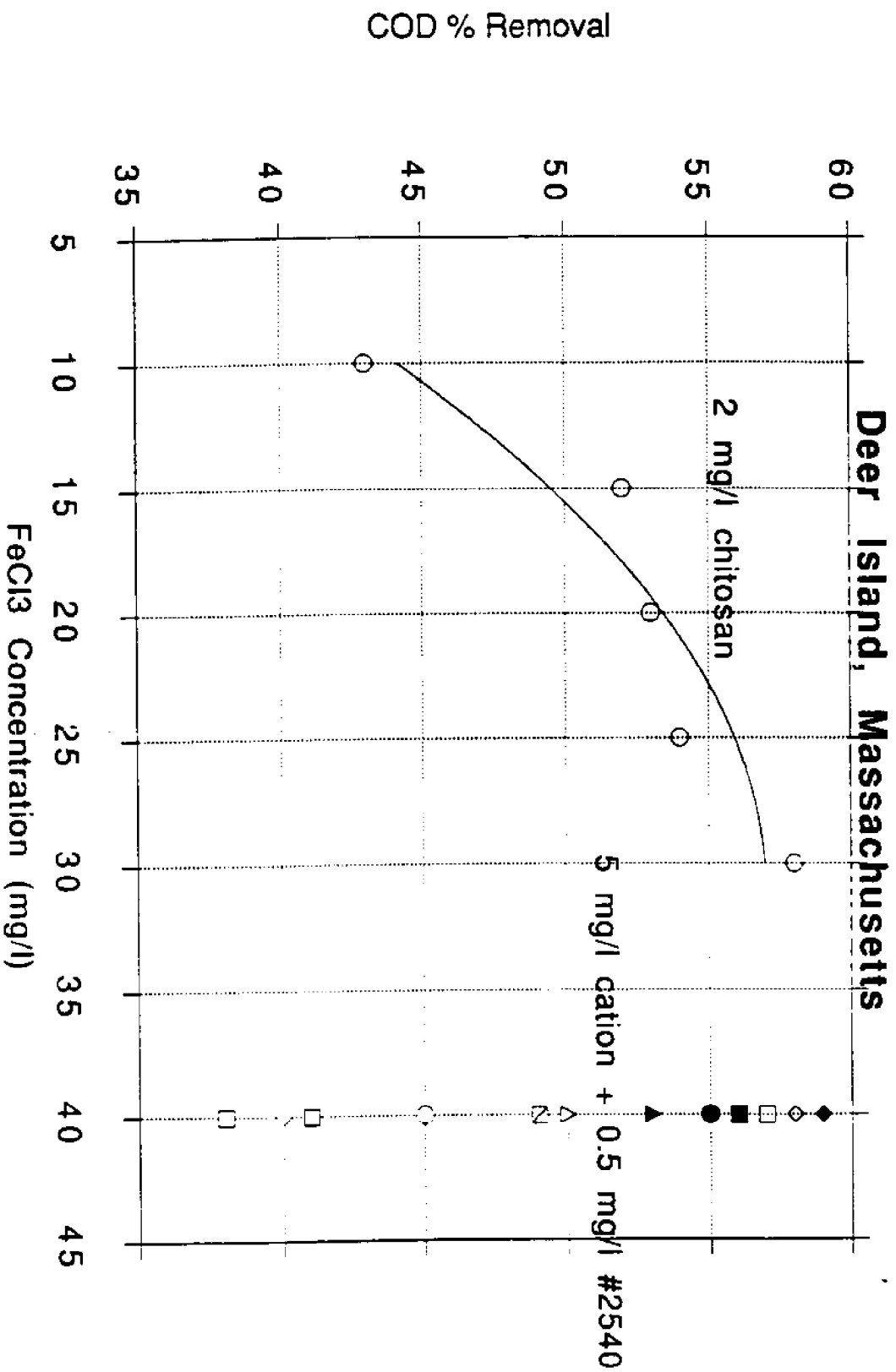


Figure 17
Comparison of Chitosan and Moringa as Coagulant Aids
COD % Removal vs. FeCl₃ Concentration
Deer Island, Massachusetts

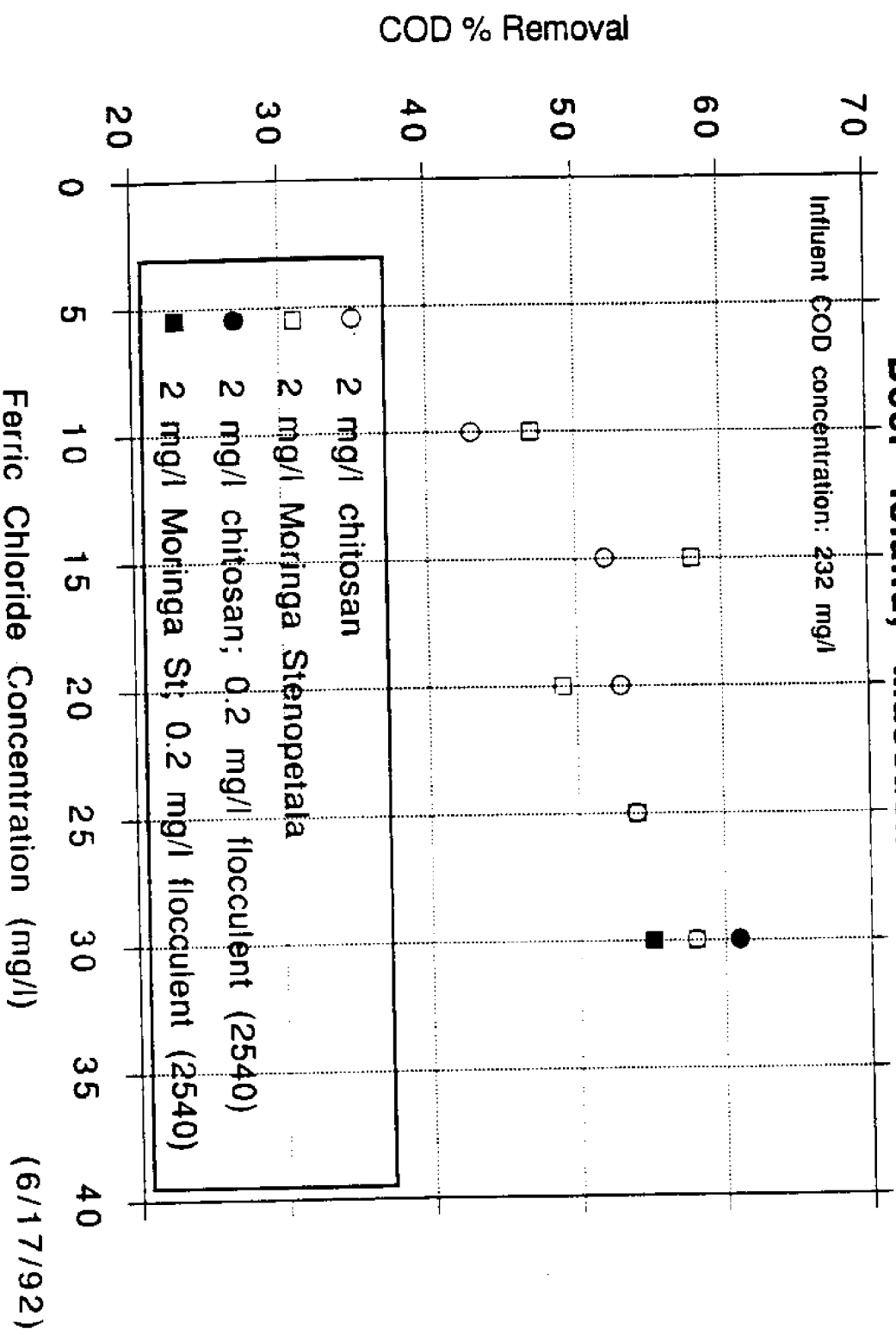


Figure 18
Comparison of 2 Moringa Species as Coagulant Aids
COD % Removal at Different FeCl₃ Concentrations
Deer Island, Massachusetts

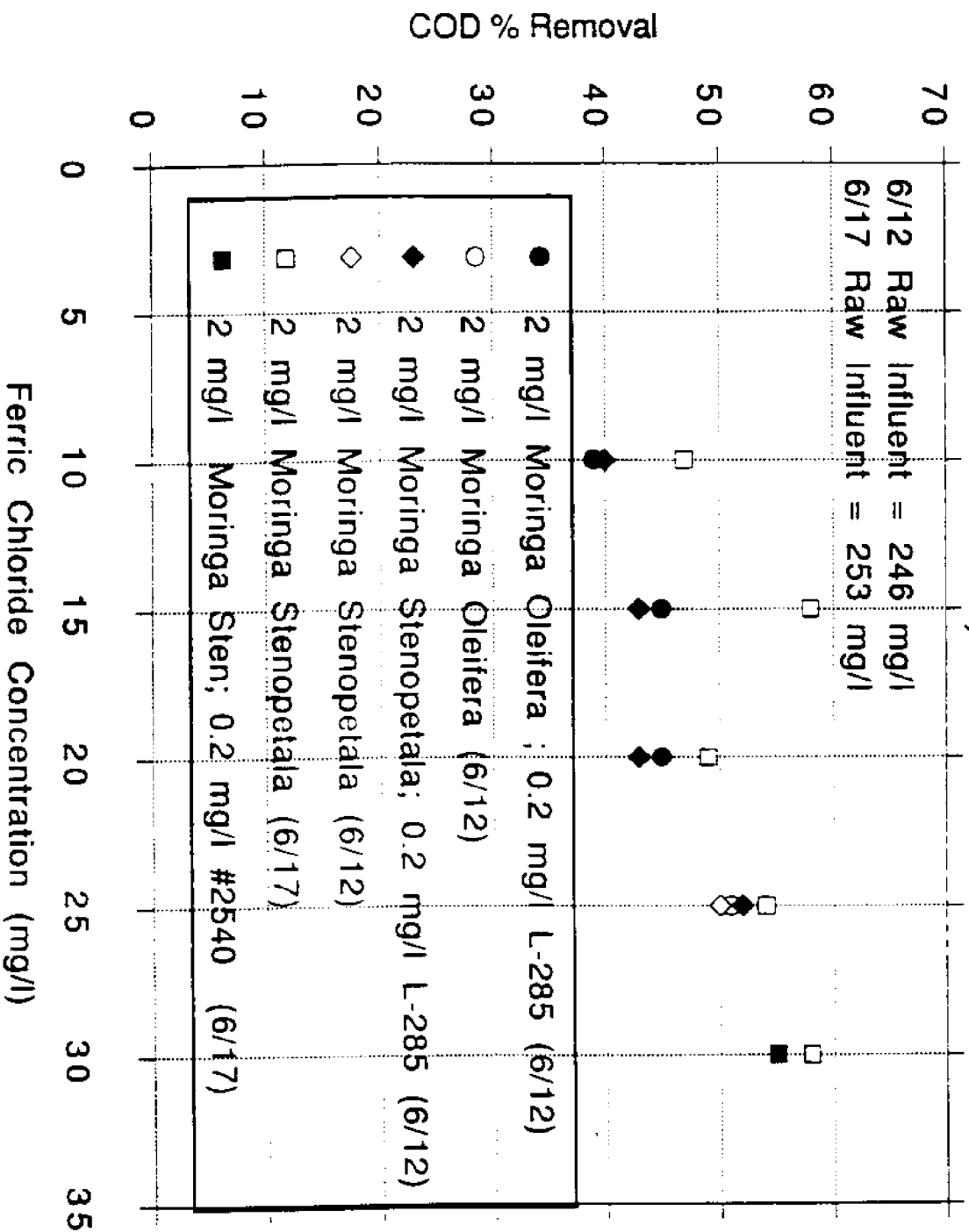


Figure 19
Chitosan as a Coagulant Aid/Flocculant
COD % Removal vs. Chitosan Concentration
Deer Island, Massachusetts

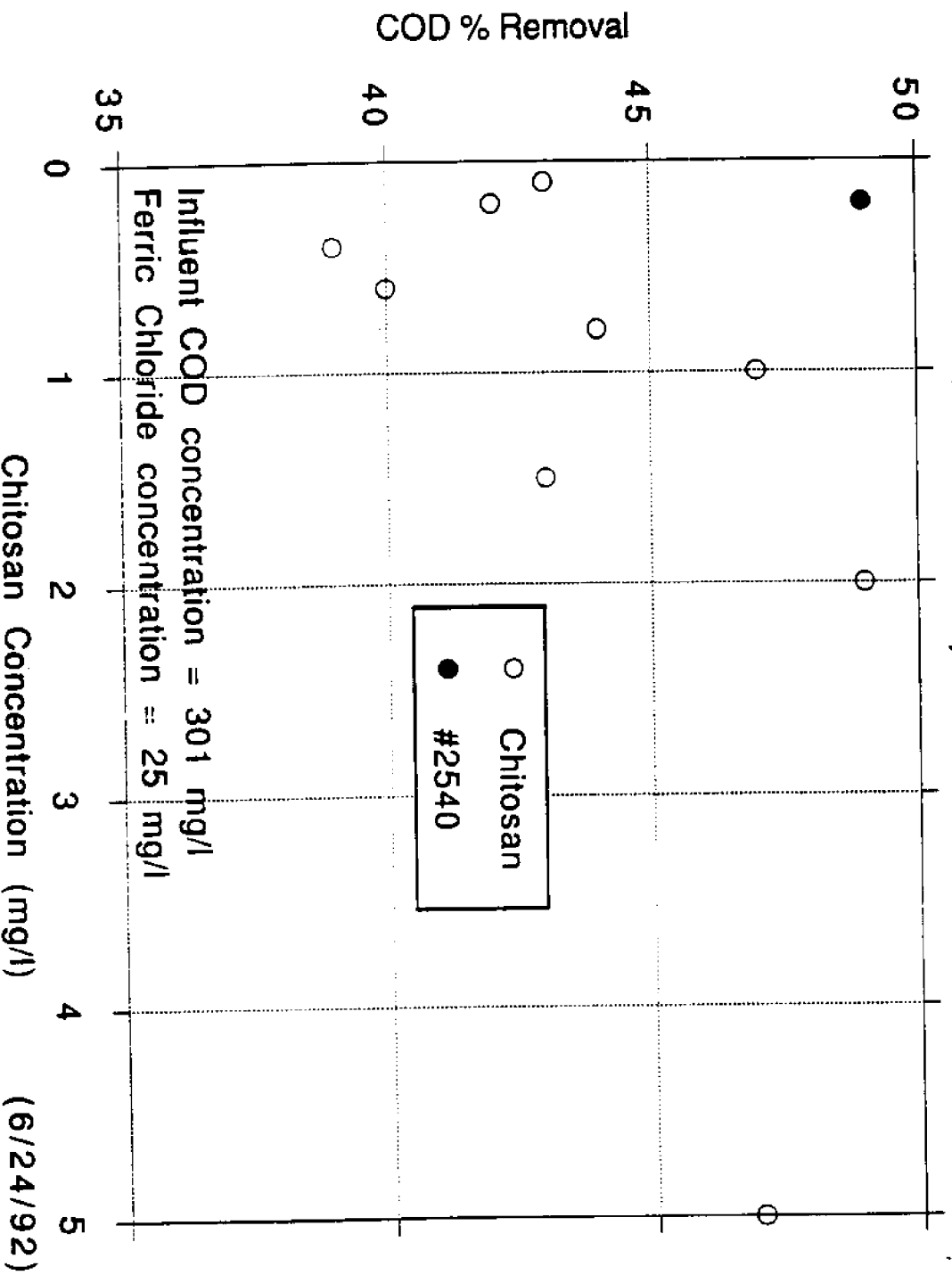
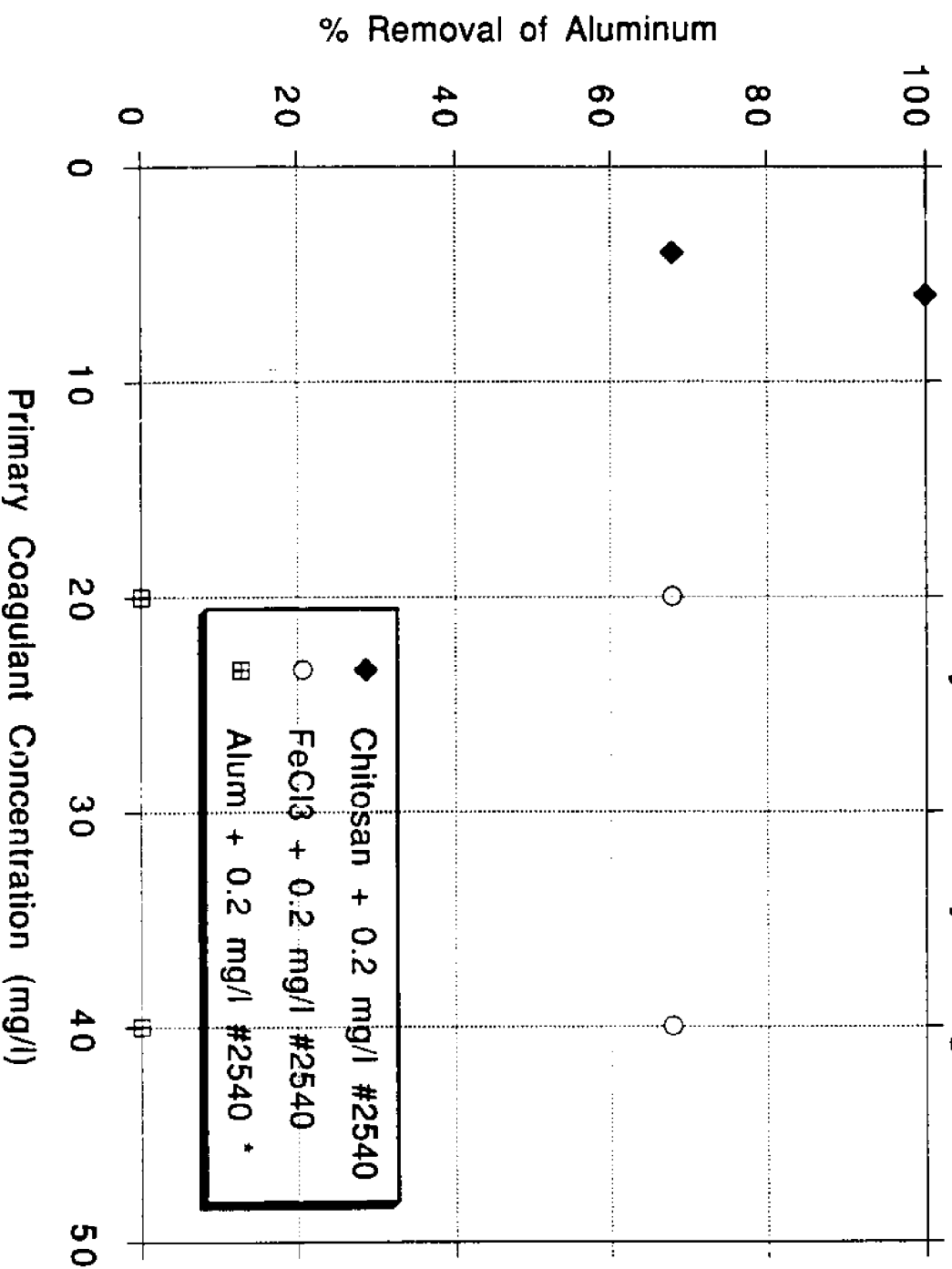


Figure 20

Aluminum Removal by 3 Primary Coagulants



* NOTE: Aluminum removal with alum is << 0.

Figure 21
Chromium Removal by 3 Primary Coagulants

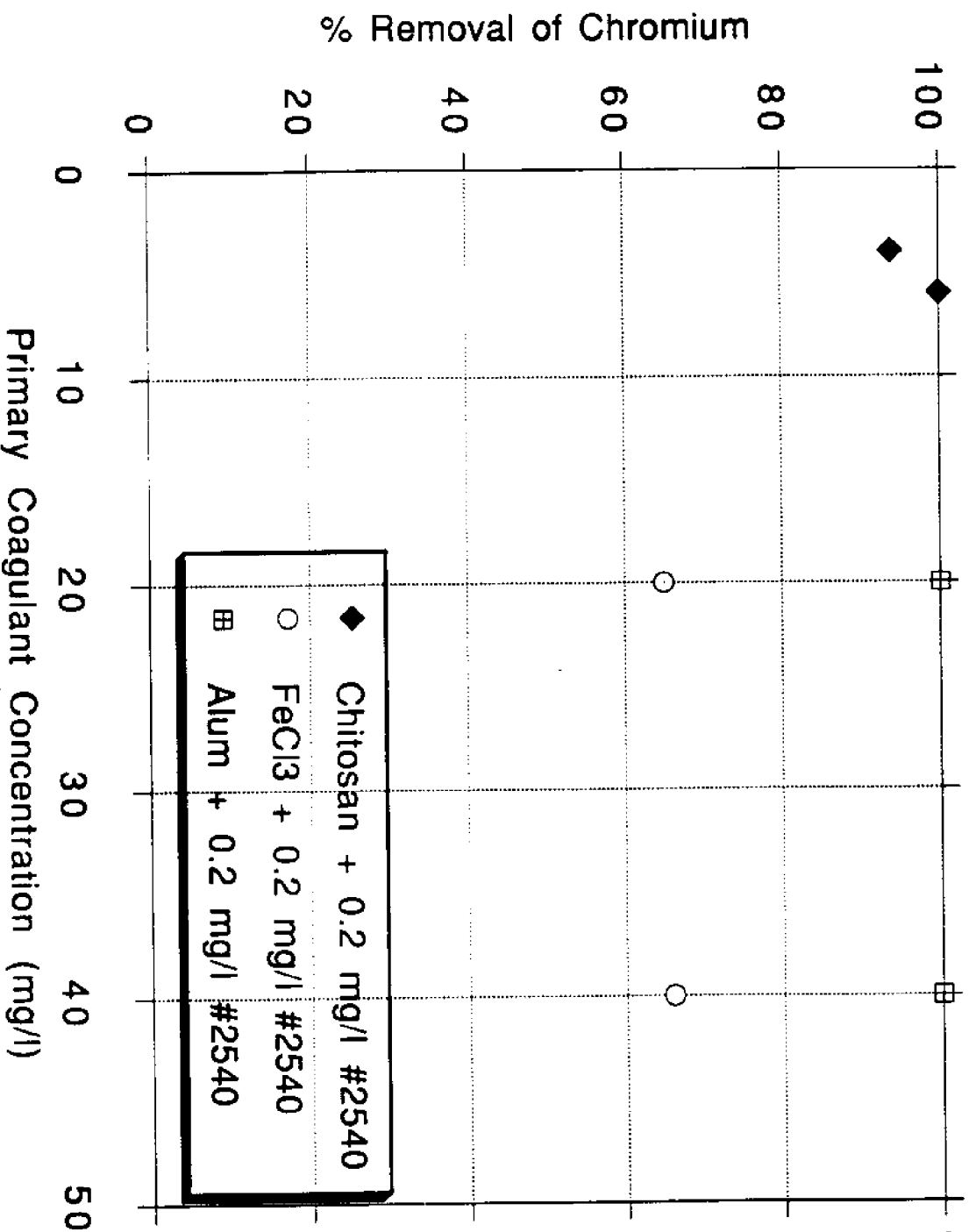


Figure 22
Copper Removal by 3 Primary Coagulants

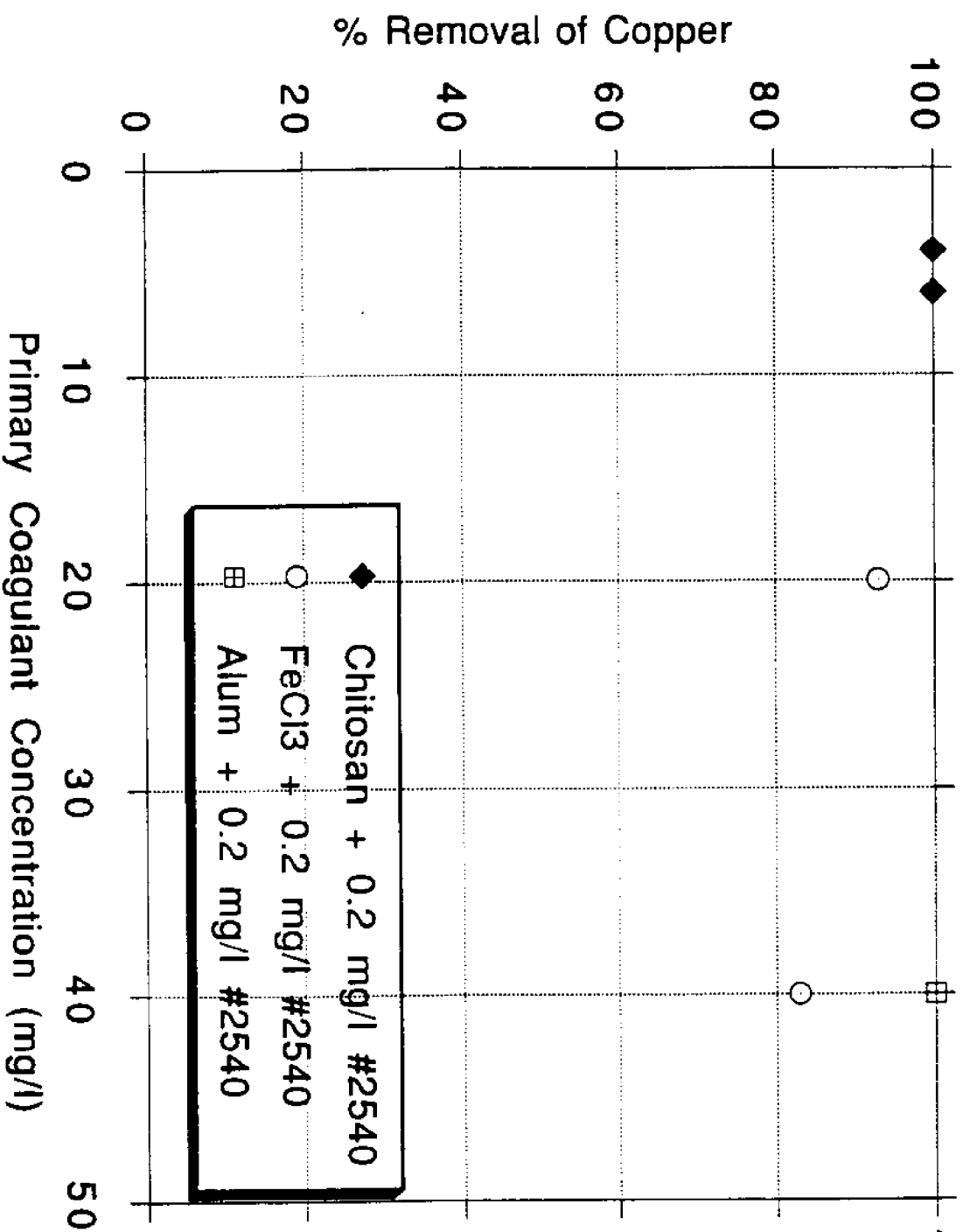


Figure 23
Iron Removal by 3 Primary Coagulants

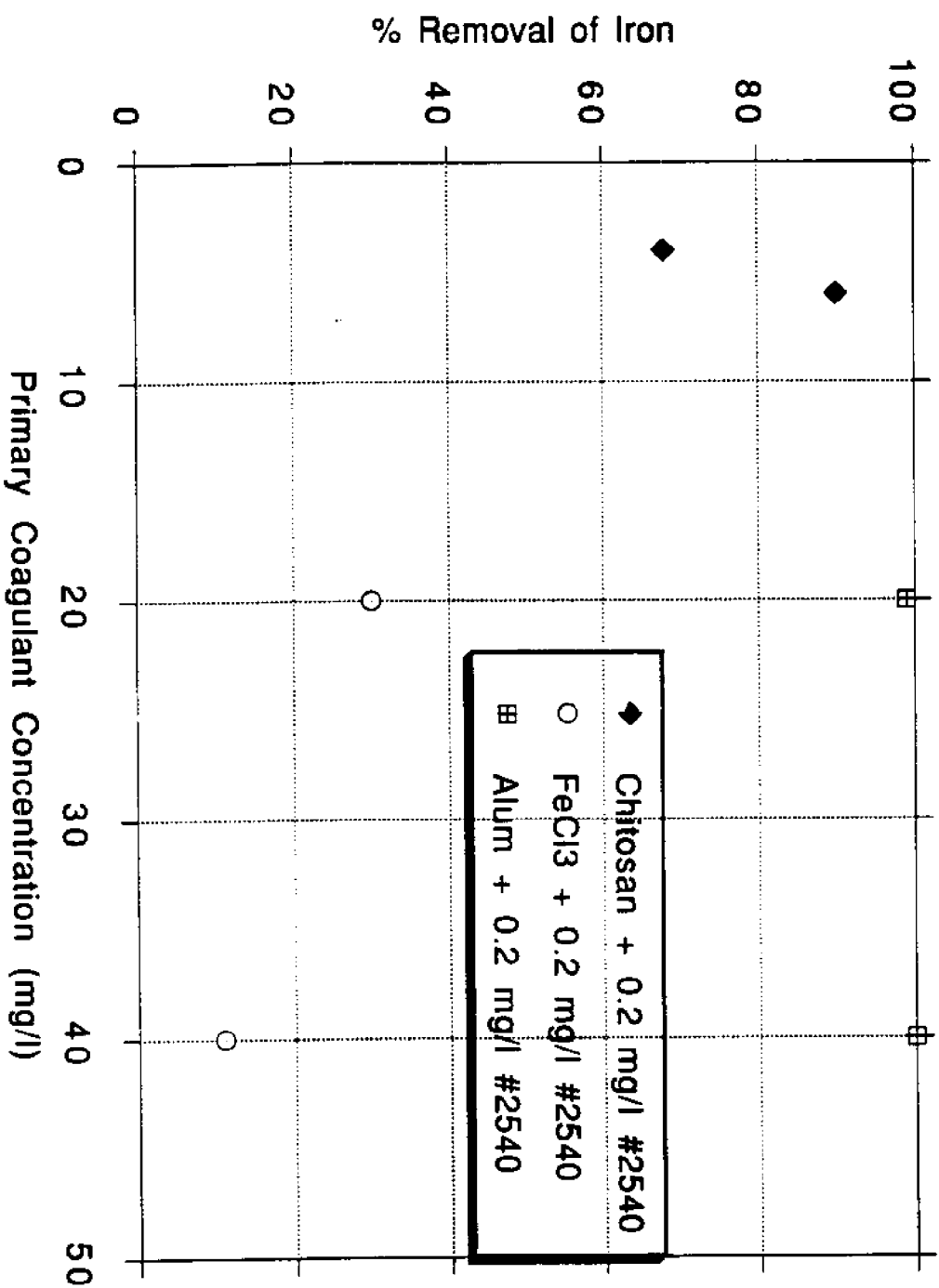


Figure 24
Manganese Removal by 3 Primary Coagulants.

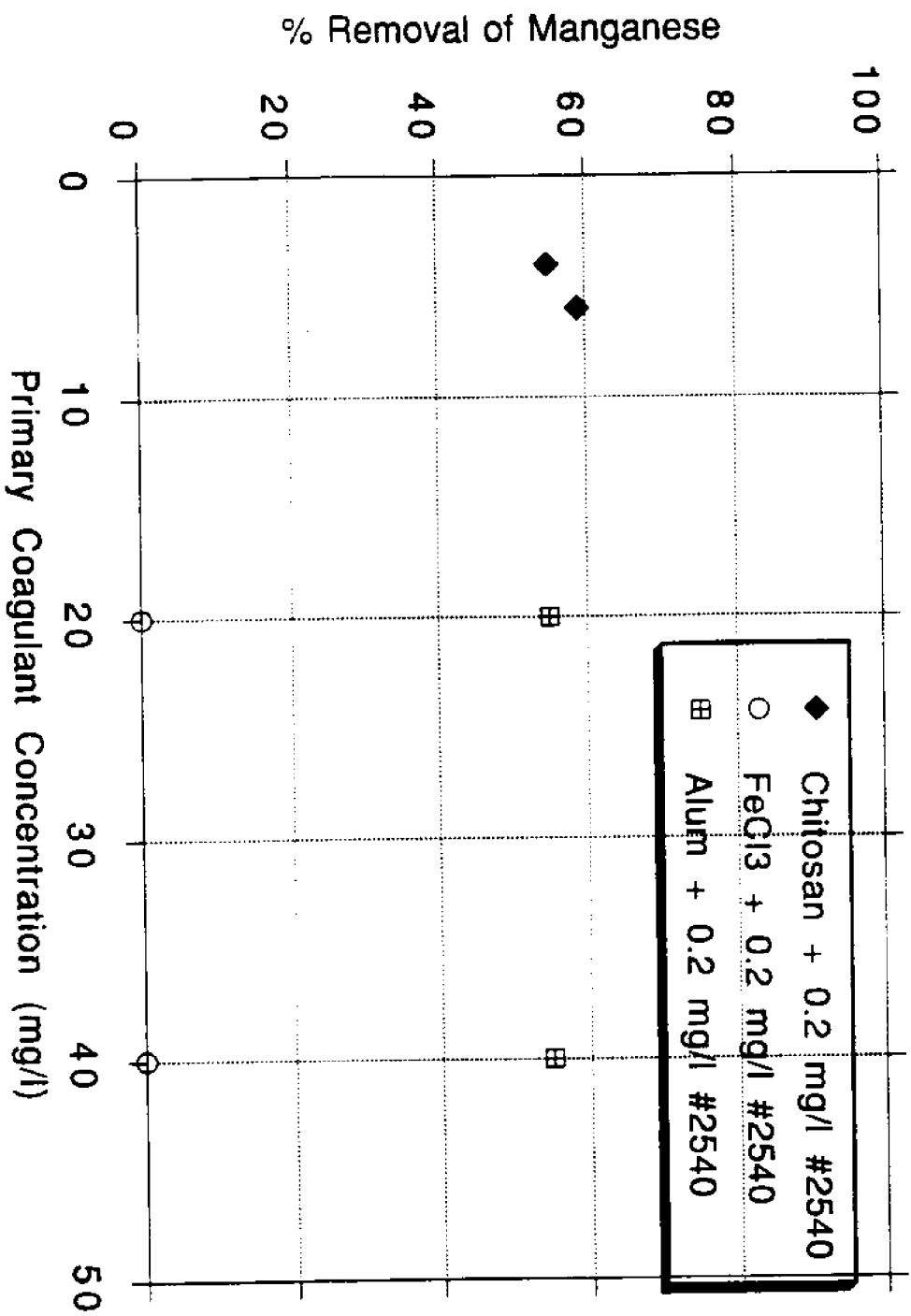


Figure 25
Silicon Removal by 3 Primary Coagulants

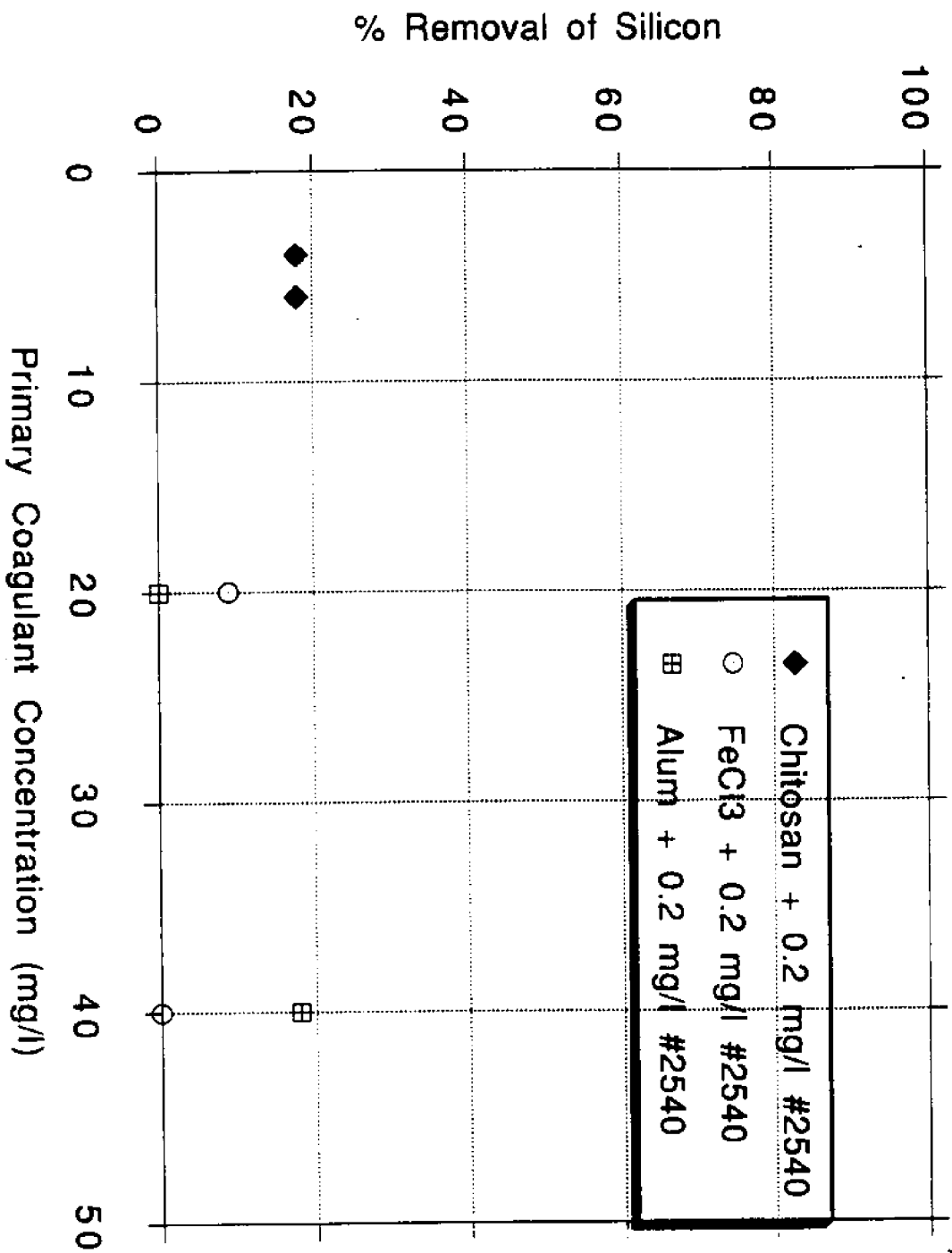


Figure 26
Chromium Removal by Ferric Chloride
and 3 Coagulant Aids

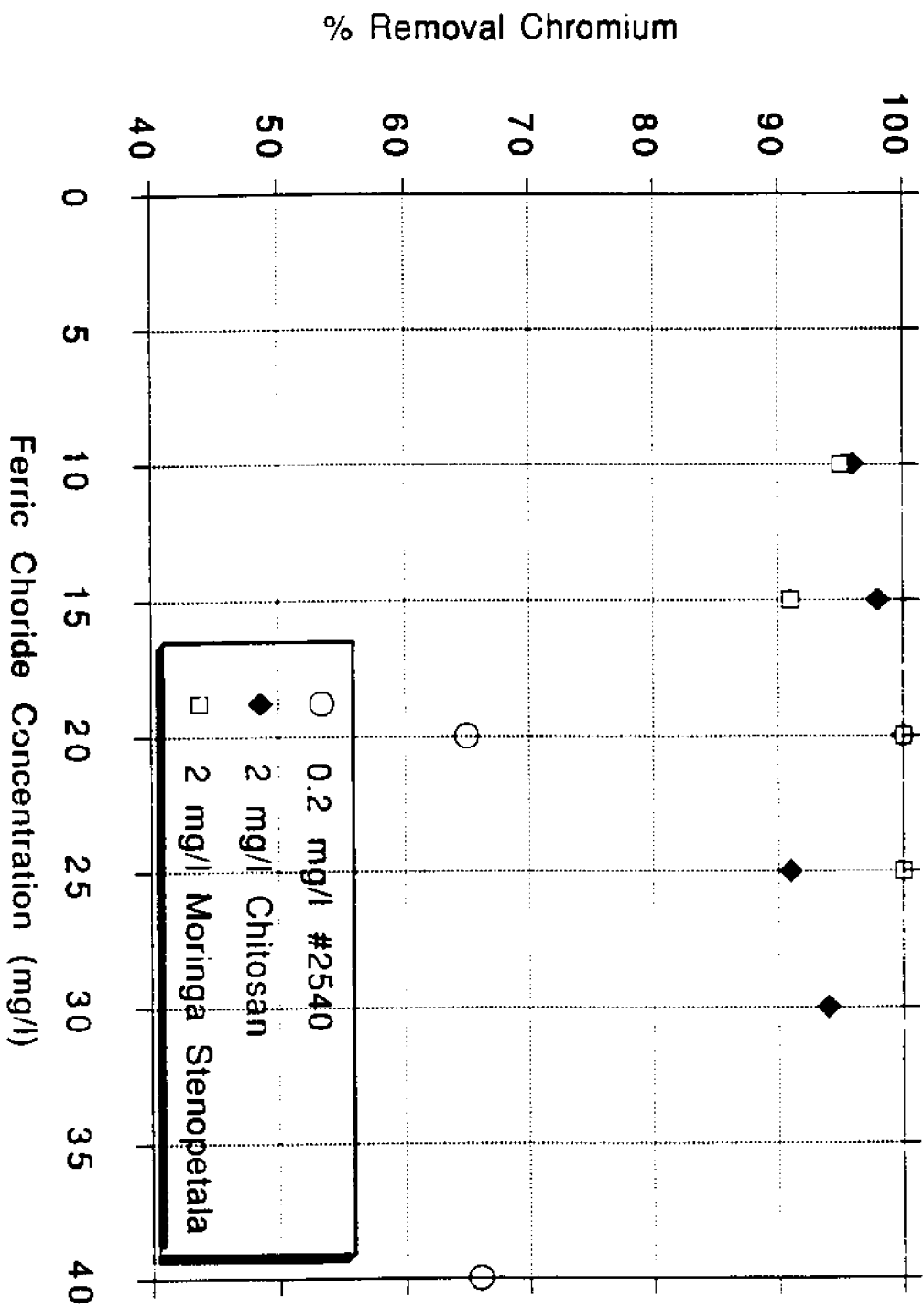


Figure 27
Copper Removal by Ferric Chloride
and 3 Coagulant Aids

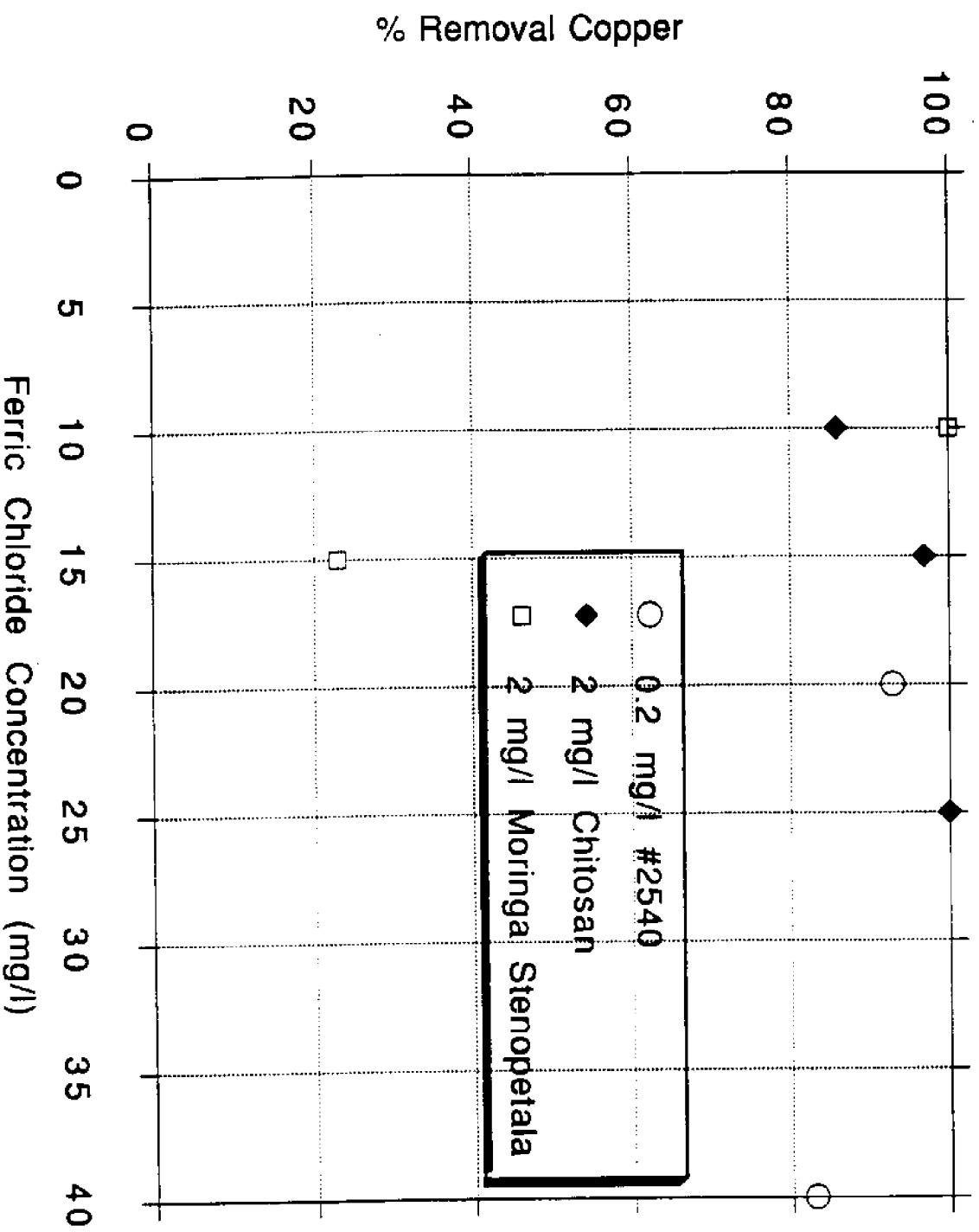
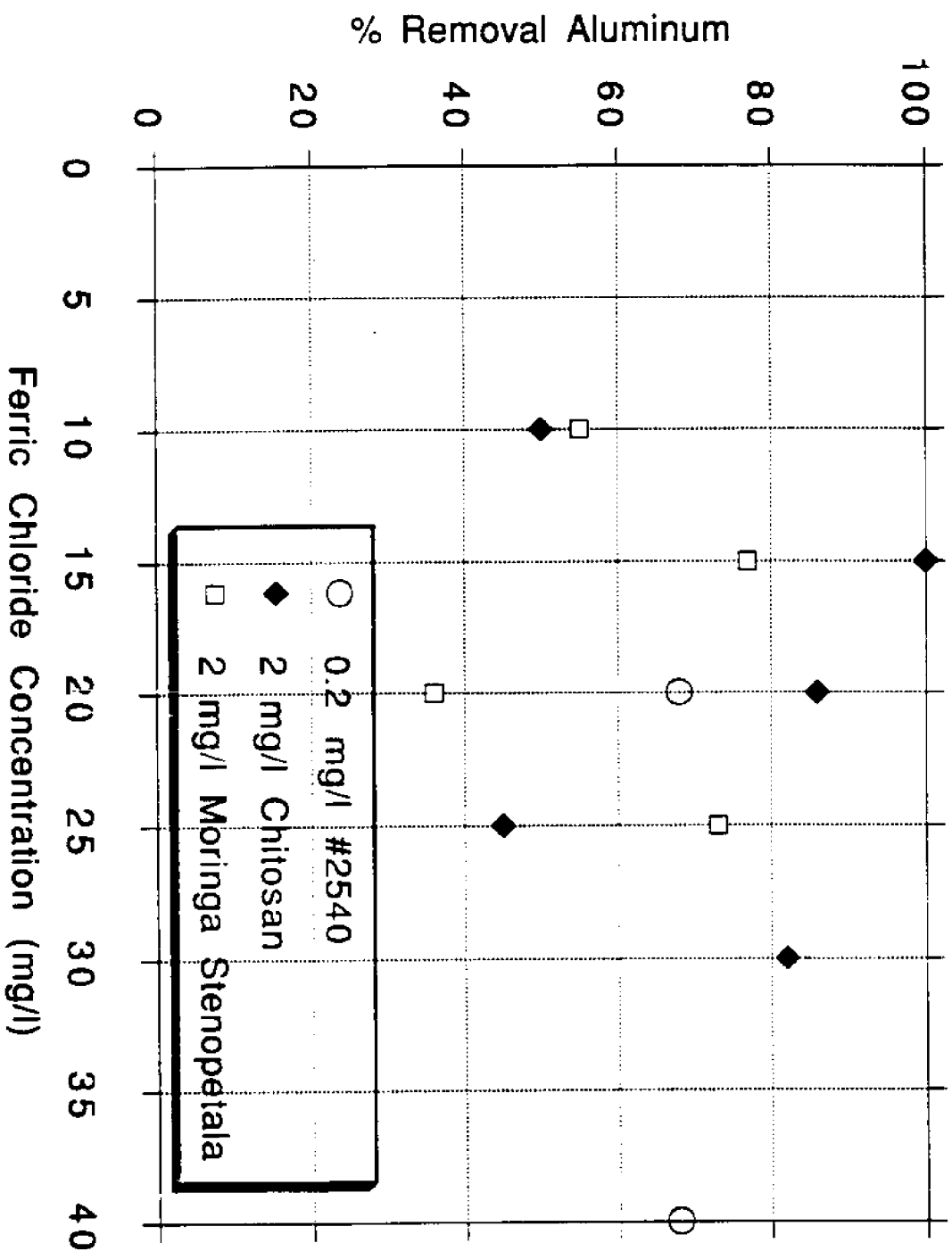


Figure 28
Aluminum Removal by Ferric Chloride
and 3 Coagulant Aids



Appendix A

Results of chitosan jar and pilot tests on wastewaters

STUDY	Chemical Dose mg/l	TSS Inf mg/l	TSS Eff mg/l	TSS Rem %	COD Inf mg/l	COD Eff mg/l	COD Rem %
1 Johnson, R.A., 1984	crab waste (jar)						
	30 ch	360	7	98			
	500 FeSO ₄	360	25	93			
	salmon waste (jar)						
	30 ch	1,350	27	98			
	500 FeSO ₄	1,350	27	98			
	shrimp waste (jar)						
	30 ch	833	17	98			
	500 FeSO ₄	833	17	98			
	crab waste underflow						
	30 ch	1,640	66	96			
	500 FeSO ₄	2,536	25	99			
	salmon waste underflow						
	30 ch	9,168	183	98			
	500 FeSO ₄	8,950	90	99			
	shrimp waste underflow						
2 Bough, W.A., 1975	30 ch	5,860	117	98			
	500 FeSO ₄	6,390	64	99			
	pimiento wastes						
	40ch	248	10	96			
	40ch + 40 alum	248	9	96			
	10ch	32	5	84			
	10 ch + 20 alum	32	5	84			
	10ch + 40 alum	32	0	100			
	20ch	75	8	89			
	30ch + 40FeCl ₃	75	0	100			
	dunker waters* (jar)						
	10ch + 15carr	256	11	96			
	dunker (pilot)						
	10ch + 15carr	1,624	6	100	2,394	915	62
	tumbler waters** (jar)						
	5ch + 10carr	1,292	132	90			
	tumbler (pilot)						
	5ch + 10carr	1,747	125	93	1,700	1,530	10
	spinach (jar)						
	20ch	298	29				
	spinach (pilot)						
	10ch + 160FeCl ₃	269	6	98	901	583	35
	turnip greens (jar)						
	10ch	143	15	90			
	green bean (jar)						
	5ch + 80CaCl ₂	116	6	95			

NOTE: ch = chitosan; carr = carrageenan

TABLE I-7
KEY U.S. PRODUCERS OF COAGULANTS DERIVED FROM NATURAL PRODUCTS

Company	Product
CPC International Inc.	a
Staley Manufacturing Corp.	a
Harvest Queen Mill and Elevator Co.	a
Celanese Corp.	b
General Mills Chemicals, Inc (Henkel K.G. a.A.)	b
Hercules	b
Swift & Co. (sub. Esmark, Inc.)	c

a = starch derivatives; b = guar gum derivatives; c = technical gelatin

Factors Influencing Chitosan Cost-Effectiveness:

1. Low dose of chitosan relative to metal salts
 - > Cost advantage for chitosan
 - > Lower chitosan sludge production relative to metal salt sludge
2. Sludge handling and disposal costs of metal salt sludges
3. Chitosan may be used to substitute for some portion of metal salt concentration if a reduction rather than an elimination of metal salt sludge is desired.

APPENDIX B

SOLUTION MAKE-UP PROCEDURE

0.8 % chemical solution -> 10 ppm per ml added
0.08% chemical solution -> 1 ppm per ml added
0.008% chemical solution -> 0.1 ppm per ml added

Metal salts and chitosan usually mixed at 0.8%.
Coagulant aids (cationic polymers) usually mixed at 0.08%.
Flocculants usually mixed at 0.008%.

Item: Chitosan

Make up 1% acetic acid solution using tap water. Then make up a 0.8% solution by adding 1.6 grams chitosan to 200 ml 1% acetic acid solution. The acetic acid facilitates the dissolution of the chitosn flakes.

Item: Carrageenan

Type 1: Puregell 400 (Semi-refined kappa carrageenan with about 10% water insoluble cellulose)
Type 2: Bengel WG 2000 (Fully refined carrageenan with neglibible water insoluble material)

Make up 0.08% carrageenan solution or less. Add 5% sodium chloride (NaCl) to water in which carrageenan is being dissolved and heat brine to 70 degrees Centigrade to be sure the carrageenan goes into solution. The NaCl suppresses the tendency of the carrageenan to gel.

Item: Alginate

Follow makeup procedure of carrageenan, with and without NaCl.

Item: Moringa oleifera

Crush the seed kernal in a pestle and mortar and dissolve in tap water to make up a 0.8% solution. Seeds should be very finely pulverized. Add 1.6 grams seed powder to 200 ml tap water. Sieve the solution so that the larger seed particles do not block pipettes or dosing apparatus. Seed solutions found to deteriorate in effectiveness with time. Seed preparations should be made up fresh before each use.

;

Study	Chemical Dose mg/l	TSS Inf mg/l	TSS Eff mg/l	TSS Rem %	COD Inf mg/l	COD Eff mg/l	COD Rem %
3 Bough, W.A., 1975 eggbreaking waste	150 ch + 10 anion	1,610	450	72	29,000	7,000	76
	150ch + 10 anion	1,930	177	91	29,000	11,000	62
	200ch + 15anion	1,005	256	75	20,900	8,900	57
	100ch + 20anion	5,027	287	94	35,000	14,250	60
4 Bough, W.A., 1976 meat packing (pilot)	30ch	465	49	89	1,800	800	56
meat packing (batch)	5ch			92			79
meat packing (pilot)	10ch + 40FeCl3	169	8	95	865	240	72
shrimp (pilot)	10ch + 5anion	2,808	178	94	6,500	1,560	76
shrimp w/DAF	100ch + 5anion	1,900	33	98	3,400	280	92
fruit cake waste	2ch	522	33	94	3,150	1,660	47
fruit cake w/DAF	2ch	158	98	38	113	93	18
5 Murcott, S.E., 1991 GWPCF municipal ww	see report						

NOTE: ch = chitinogen; carr = carrageenan;

APPENDIX C
JAR TEST PROCEDURE

1. Place 800 ml wastewater sample in each of the six 1000 ml beakers.
2. Add primary coagulant and stir at 100 rpms for 30 seconds.
3. Add coagulant aid (if desired). Stir at 60 rpms for 2 minutes.
4. Add flocculent (if desired).
5. Rapid mix (100 rpms) flocculent for 10 seconds.
6. Stir at slow speed of 20 rpms for 1 minute.
7. Stop. Allow mixture to settle for 5 minutes.
8. Draw samples from upper half of the beaker using a 60 cc syringe, taking care not to stir up the sediment.

Item: *Moringa stenopetala*

Crush the seed kernal in a pestle and mortar and dissolve in tap water to make up a 1% solution. Seeds should be very finely pulverized. Add 1.6 grams seed powder to 200 ml tap water. Sieve the solution so that the larger seed particles do not block pipettes or dosing apparatus. Seed solutions found to deteriorate in effectiveness with time. Seed preparations should be made up fresh before each use.

Item: *Strychnos potatorum*

Break up the seed kernal by filing (more effective with this seed than crushing) and dissolve in tap water to make up a 1% solution. Seeds should be very finely pulverized. Add 1.6 grams seed powder to 200 ml tap water. Sieve the solution so that the larger seed particles do not block pipettes or dosing apparatus. Seed solutions found to deteriorate in effectiveness with time. Seed preparations should be made up fresh before each use.

APPENDIX E
BATCH TEST PROCEDURE FOR PAH TESTING AT DEER ISLAND

PAH testing of samples taken at Deer Island for coagulant and flocculent testing requires the use of 10 gallon plastic or metal containers mixed by a stirrer driven by an electric power drill. The speed control mechanism of the drill is not precise; only slow, medium and fast speed delineations can be made. The following procedure should be followed to simulate jar test mixing conditions.

1. Using an indelible marker, note the water level on the container's inner wall corresponding to 30 liters (7.9 gal). Use this mark as a reference for future samples.
2. Fill the container with 30 liters (7.9 gal) raw sample water.
3. Mount the wooden drill holder, along with the drill, on top of the container so that the drill shaft is properly centered. (Note: Make sure the shaft is securely fastened to the drill).
4. Stir the raw sample for 30 seconds to make sure it is well mixed.
5. Using a syringe (or measuring pipette), add the test quantity of coagulant to the sample at the center of the container. (Avoid adding the coagulant directly on the stirrer; improper dosage may result).
6. Mix for 30 seconds at high speed (approximately 100 rpms).
7. Reduce stirrer to medium speed (approximately 60 rpms) and mix for 2 minutes. If a coagulant aid is also used, add at half-way point (i.e., after 1 minute). Mix at high speed (100 rpms) for 10 seconds, and then resume medium speed (60 rpms) for remainder for 2 minutes.
8. If a flocculent is used, add flocculent and mix at high speed (100 rpms) for 10 seconds.
9. Reduce to slow speed (20 rpms) and mix for 2 additional minutes.
10. Stop all mixing and allow 20 minutes for floc to settle.
11. Decant 17.1 liters (4.5 gallons) into cleansed 1-gallon bottles.
12. Repeat entire procedure once to obtain 34.2 liters (9 gallons) PAH sample.

Table One: Trial Preliminary Final Confirmation

Jar	Chemicals Used & Concentration (mg/l)				Color	pH	TSS (mg/l)	Clarity and Visual Observations
	Time	Alum	Ferric	Anionic				
1								
2								
3								
4								
5								
Control								
6	0	0	0	0				

Polymer Manufacturer: _____

Comments:

Sequence/Time of Chemical Addition:

Mixing:
 Min. @ _____ RPM

DEER ISLAND NATURAL POLYMERS STUDY
TEST RESULTS -- MAY 28, 1992

#	Primary Coagulant	mg/l	Coagulant Aid	mg/l	Flocculent	mg/l	COO mg/l	COO %
1	Raw Influent						253	
2	Zero						238	
3	FeCl3	20			2540	0.2	135	47
4	FeCl3	30			2540	0.2	123	51
5	FeCl3	40			2540	0.2	118	53
6	FeCl3	20	Ch	5	2540	0.2	136	46
7	FeCl3	30	Ch	5	2540	0.2	123	51
8	FeCl3	40	Ch	5	2540	0.2	123	51
9	Fe(SO4)4	20			2540	0.2	160	37
10	Fe(SO4)4	30			2540	0.2	142	44
11	Fe(SO4)4	40			2540	0.2	138	45
12	Fe(SO4)4	20	Ch	5	2540	0.2	172	32
13	Fe(SO4)4	30	Ch	5	2540	0.2	161	36
14	Fe(SO4)4	40	Ch	5	2540	0.2	146	42
15	Alum	20			2540	0.2	162	36
16	Alum	30			2540	0.2	152	40
17	Alum	40			2540	0.2	140	45
18	Alum	20	Ch	5	2540	0.2	170	33
19	Alum	30	Ch	5	2540	0.2	160	37
20	Alum	40	Ch	5	2540	0.2	153	40

Note: Ch = chitosan; 2540 = anionic polyacrylamide.

**DEER ISLAND NATURAL POLYMERS STUDY
TEST RESULTS -- MAY 29, 1992**

#	Primary Coagulant	mg/l	Flocculent	mg/l	TSS mg/l	TSS %	COD mg/l	COD %
1	Raw Influent				141		262	
2	Raw Influent				150		265	
	Ave. Influent				145		263	
3	Zero				130	10	257	2
4	Ch	1	2540	0.2	127	12	242	8
5	Ch	2	2540	0.2	107	26	221	16
6	Ch	3	2540	0.2	115	21	209	21
7	Ch	4	2540	0.2	120	17	198	25
8	Ch	5	2540	0.2	100	30	199	25
9	Ch	6	2540	0.2	100	31	204	23
10	Ch	8	2540	0.2	112	23	210	20
11	Ch	10	2540	0.2	112	23	221	16
12	Ch	12	2540	0.2	106	27	223	17
13	Ch	14	2540	0.2	97	33	232	12
14	Ch	16	2540	0.2	99	32	237	10

**DEER ISLAND NATURAL POLYMERS STUDY
TEST RESULTS -- MAY 29, 1992**

#	Primary Coagulant	mg/l	Flocculent	mg/l	TSS mg/l	TSS %
1	Raw Influent				148	
2	Raw Influent				146	
	Ave. Influent				147	
3	Zero				113	23
4	FeCl3	5	2540	0.2	103	30
5	FeCl3	10	2540	0.2	99	33
6	FeCl3	15	2540	0.2	92	37
7	FeCl3	20	2540	0.2	85	42
8	FeCl3	25	2540	0.2	83	44
9	FeCl3	30	2540	0.2	71	52
10	FeCl3	40	2540	0.2	58	61
11	FeCl3	50	2540	0.2	58	61
12	FeCl3	60	2540	0.2	44	70
13	FeCl3	70	2540	0.2	44	70
14	FeCl3	80	2540	0.2	42	71

Note: Ch = chitosan; 2540 = anionic polyacrylamide

**DEMINERALIZED WATER
TEST RESULTS -- MAY 30, 1992**

#	Primary Coagulant	mg/l	COD (mg/l)
1	FeCl3	5	0
2	FeCl3	10	0
3	FeCl3	25	0
4	Ch	5	12
5	Ch	10	50
6	Ch	25	88

Note: Ch = chitosan.

**DEER ISLAND NATURAL POLYMERS STUDY
COD RESULTS -- JUNE 11, 1992**

Coagulant	Conc. (mg/l)	Coagulant Aid	Conc. (mg/l)	Flocculent	Conc. (mg/l)	COD (mg/l)	COD % Removal
Raw Influent						327	
Ch	5			2540	0.2	170	48
Ch	5			S-42	0.2	164	50
Ch	5			K-347	0.2	174	47
Ch	5			N-415	0.2	165	50
Ch	5			N-417	0.2	163	50
Ch	5			L-285	0.2	162	50
Ch	5			2540	0.5	153	53
Ch	5			S-42	0.5	185	43
Ch	5			L-285	0.5	176	46
Ch	5	M.S.	1	2540	0.2	161	51
Ch	5	M.S.	2	2540	0.2	167	49
Ch	4	M.S.	6	2540	0.2	170	48
Raw Influent						396	
Ch	5	M.S.	1	2540	0.2	142	64
Ch	5	M.S.	1	S-41	0.2	166	58
Ch	5	M.S.	1	L-285	0.2	134	66
Ch	5	M.S.	1	L-285	0.1	212?	46
Ch	5	M.O.	1	L-285	0.05	209	47
Ch	5	M.O.	1	L-285	0.01	226	43

NOTE: Ch = chitosan; M.S. = moringa stenopetala; M.O. = moringa oleifera.

DEER ISLAND NATURAL POLYMERS STUDY
COD RESULTS -- JUNE 12, 1992

Coagulant	Conc. (mg/L)	Coagulant Aid	Conc. (mg/L)	Flocculent	Conc. (mg/L)	COD (mg/L)	COD % Removal
Raw Influent						243	
Raw Influent						248	
Ave. Influent						246	
FeCl ₃	20	Ch	0.2	L-285	0.2	124	50
FeCl ₃	20	Ch	2	L-285	0.2	134	46
FeCl ₃	20	Ch	2	-	-	128	48
FeCl ₃	5	Ch	2	L-285	0.2	160	35
FeCl ₃	10	Ch	2	L-285	0.2	121	51
FeCl ₃	15	Ch	2	L-285	0.2	114	54
FeCl ₃	20	Ch	2	L-285	0.2	120	51
FeCl ₃	25	Ch	2	L-285	0.2	105	57
FeCl ₃	25	Ch	2	-	-	111	55
Raw Influent						313	
Raw Influent						317	
Ave. Influent						315	
FeCl ₃	10	M.O.	2	L-285	0.2	193	39
FeCl ₃	15	M.O.	2	L-285	0.2	173	45
FeCl ₃	20	M.O.	2	L-285	0.2	173	45
FeCl ₃	25	M.O.	2	L-285	0.2	145	54
FeCl ₃	25	M.O.	2	-	-	155	51
FeCl ₃	10	M.S.	2	L-285	0.2	189	40
FeCl ₃	15	M.S.	2	L-285	0.2	180	43
FeCl ₃	20	M.S.	2	L-285	0.2	180	43
FeCl ₃	25	M.S.	2	L-285	0.2	152	52
FeCl ₃	25	M.S.	2	-	-	156	50

NOTE: Ch = chitosan; M.S. = moringa stenopetala; M.O. = moringa oleifera.

DEER ISLAND NATURAL POLYMERS STUDY
COD RESULTS -- JUNE 16, 1992

Coagulant	Conc. (mg/l)	Coagulant Aid	Conc. (mg/l)	Flocculent	Conc. (mg/l)	COD (mg/l)	COD % Removal
Raw Influent						196	
Raw Influent						215	
Ave. Influent						206	
Ch	0.5			L-285	0.2	198	4
Ch	1			L-285	0.2	184	11
Ch	2			L-285	0.2	183	11
Ch	3			L-285	0.2	167	19
Ch	4			L-285	0.2	216	- 5
Ch	5			L-285	0.2	194	6
Ch	6			L-285	0.2	200	3
Ch-1 hour	6			L-285	0.2	173	16
Ch	7			L-285	0.2	181	12
Ch	8			L-285	0.2	193	6
Ch	9			L-285	0.2	184	11
Ch	10			L-285	0.2	195	5
FeCl3	10	Ch	2	L-285	0.2	161	22
FeCl3	15	Ch	2	L-285	0.2	158	23
FeCl3	20	Ch	2	L-285	0.2	136	34
FeCl3	25	Ch	2	L-285	0.2	147	29
FeCl3	30	Ch	2	L-285	0.2	125	39
FeCl3	35	Ch	2	L-285	0.2	127	38
FeCl3	10	Ch	2	-	-	171	17
FeCl3	15	Ch	2	-	-	161	22
FeCl3	20	Ch	2	-	-	149	28
FeCl3	25	Ch	2	-	-	128	38
FeCl3	30	Ch	2	-	-	133	35
FeCl3	35	Ch	2	-	-	118	43

NOTE: Ch = chitosan; M.S. = moringa stenopetala; M.O. = moringa oleifera.

DEER ISLAND NATURAL POLYMERS STUDY
TEST RESULTS -- JUNE 17, 1992

#	Primary Coagulant	mg/l	Coagulant Aid	mg/l	Flocculent	mg/l	TSS mg/l	TSS %	COO mg/l	COO %
1	Raw Influent						88,106		253, 218	
2	Raw Influent						89,82		226	
	Ave. Influent						91		232	
3	Zero						67	26	169,159 Ave = 164	29
4	FeCl3	20			2540	0.2	42	54	95	59
5	FeCl3	40			2540	0.2	34	63	81	65
6	Alum	20			2540	0.2	37	59	113	51
7	Alum	40			2540	0.2	25	73	80	66
12	FeCl3	10	Ch	2			44	52	135	42
13	FeCl3	15	Ch	2			41	55	114	51
14	FeCl3	20	Ch	2			48	47	110	53
15	FeCl3	25	Ch	2			37	59	110, 108	53
16	FeCl3	30	Ch	2			45	51	98	58
17	FeCl3	30	Ch	2	2540	0.2	41	55	92	60
18	FeCl3	10	M.S.	2			51	44	125	46
19	FeCl3	15	M.S.	2			26	71	98	58
20	FeCl3	20	M.S.	2			28	69	121	48
21	FeCl3	25	M.S.	2			39	57	109	53
22	FeCl3	30	M.S.	2			36	60	98	58
23	FeCl3	30	M.S.	2	2540	0.2	20	78	107	54

Note: Ch = chitosan, M.S. = moringa stenopetala, 2540 = anionic polyacrylamide of 40 mole charge percent.

**DEER ISLAND NATURAL POLYMERS STUDY
TEST RESULTS - JUNE 17, 1992**

#	Primary Coagulant	mg/l	Coagulant Aid	mg/l	Flocculent	mg/l	TSS mg/l	TSS %	COD mg/l	COD %
24	Ch	1			2540	0.2	54	41	150	35
25	Ch	2			2540	0.2	58	36	164	29
26	Ch	3			2540	0.2	56	38	155	33
27	Ch	4			2540	0.2	56	38	163	30
28	Ch	5			2540	0.2	75	18	164, 169	28
29	Ch	6			2540	0.2	49	46	151, 154	34
30	Ch	5	M.S.	1			57	37	160	31
31	Ch	5	M.S.	2			55	40	168	28
32	Ch	5	M.S.	1	2540	0.2	50	45	168	28
33	Ch	5	M.S.	2	2540	0.2	50	45	167, 177	26
34	Alum	20	M.S.	2			69	24	162	30
35	Alum	20	Ch	2			51	44	146, 145	37

Note: Ch = chitosan, M.S. = moringa stenopetala, 2540 = anionic polyacrylamide of 40 mole charge percent.

DEER ISLAND NATURAL POLYMERS STUDY
TEST RESULTS -- JUNE 24, 1992

#	Test		Primary Coagulant	mg/l	Flocculant	mg/l	COD mg/l	COD %
1			Raw Influent				288, 313 Ave = 301	
2	Mixing Speed	20 rpm	Ch	5	2540	0.2	212	30
3	"	40 rpm	Ch	5	2540	0.2	186	38
4	"	60 rpm	Ch	5	2540	0.2	197	35
5	"	80 rpm	Ch	5	2540	0.2	196	35
6	"	100 rpm	Ch	5	2540	0.2	169, 170	44
7	Mixing Time	0.5 min	Ch	5	2540	0.2	204	32
8	"	1 min	Ch	5	2540	0.2	211	30
9	"	2 min	Ch	5	2540	0.2	202	33
10	"	3 min	Ch	5	2540	0.2	210	30
11	"	4 min	Ch	5	2540	0.2	190 1 hr = 202	37 33
12	"	9 min	Ch	5	2540	0.2	173, 189 Ave = 181 1 hr = 167	40 45
13	Temp Variation	12 degrees C	Ch	5	2540	0.2	224	26
14		16 degrees C	Ch	5	2540	0.2	216	28
15		20 degrees C	Ch	5	2540	0.2	204	32

Note: Ch = chitosan, M.S. = moringa stenopetala, 2540 = anionic polyacrylamide of 40 mole charge percent.

DEER ISLAND NATURAL POLYMERS STUDY
TEST RESULTS -- JUNE 24, 1992

#	Test	Primary Coagulant	mg/l	Coagulant Aid	mg/l	Flocculant	mg/l	COD mg/l	COD %
		Raw Influent						288, 313 Ave = 301	
16	Ch as Flocculent	FeCl3	25			Ch	0.1	173	43
17		FeCl3	25			Ch	0.2	174	42
18		FeCl3	25			Ch	0.4	183	39
19		FeCl3	25			Ch	0.6	180	40
20		FeCl3	25			Ch	0.8	170	44
21		FeCl3	25			Ch	1.0	159	47
22		FeCl3	25			Ch	1.5	171	43
23		FeCl3	25			Ch	2.0	153	49
24		FeCl3	25			Ch	5.0	159	47
25		FeCl3	25			2540	0.2	155	49
26	Worst, Standard, Best	Ch	5			2540	0.2	227	25
27		Ch	5			2540	0.2	218	28
28		Ch	5			2540	0.2	189	40
29		Raw Influent						402, 409 Ave = 406	
30	Test MS w/ "Best"	Ch	5	M.S.	2			162	60
31		Ch	5	M.S.	2	2540	0.2	160	61

Note: Ch = chitosan, M.S. = moringa stenopetala, 2540 = anionic polyacrylamide of 40 mole charge percent.

APPENDIX G
METALS CONCENTRATION DATA
JUNE 17, 1992

Chemical Regime (Coagulant concentrations in mg/l)	Cr mg/l	Zn mg/l	Cu mg/l	Al mg/l	Ba mg/l	Fe mg/l	Si mg/l	Mn mg/l
Detection Limit	.01	.01	.01	.04	.02	.01	.02	.01
BLANK	.22	.02	.06	.12	0	1.05	.50	.02
Influent	1.08	.08	.29	.22	.05	3.65	3.3	.29
20 FeCl ₃ +0.2 #2540	.38	.04	.02	.07	.03	2.55	3.0	.56
40 FeCl ₃ +0.2 #2540	.37	ND	.05	.07	.04	3.25	3.3	.91
20 Alum+0.2 #2540	ND	ND	ND	.57	.03	.05	3.4	.13
40 Alum+0.2 #2540	ND	ND	ND	.54	.03	ND	2.7	.13
10 FeCl ₃ + 2 Ch	.04	ND	.04	.11	.03	2.15	3.2	.35
15 FeCl ₃ + 2 Ch	.02	.03	.01*	ND	.03	.95	3.0	.42
20 FeCl ₃ + 2 Ch	ND	.03	ND	ND	.02*	.55	3.0	.52
25 FeCl ₃ + 2 Ch	.10	.04	ND	.12	.03	4.05	3.3	.61
30 FeCl ₃ + 2 Ch	.06	ND	ND	.04*	.03	2.55	2.9	.72
30 FeCl ₃ + 2 Ch + 0.2 #2540	ND	ND	ND	ND	.03	.25	2.6	.62
10 FeCl ₃ + 2 M.S.	.05	ND	ND	.10	.03	2.75	2.9	.32
15 FeCl ₃ + 2 M.S.	.10	ND	.21	.05	.03	2.25	2.9	.43
20 FeCl ₃ + 2 M.S.	ND	ND	ND	.14	.03	1.85	2.9	.47
25 FeCl ₃ + 2 M.S.	ND	ND	ND	.06	.03	1.15	3.0	.56
30 FeCl ₃ + 2 M.S.	ND	ND	ND	ND	ND	ND	ND	ND
30 FeCl ₃ + 2 M.S.+ 0.2 #2540	ND	ND	ND	ND	ND	ND	ND	ND
1 Ch + 0.2 #2540	ND	ND	ND	ND	ND	ND	ND	ND
2 Ch + 0.2 #2540	ND	ND	ND	ND	ND	ND	ND	ND
3 Ch + 0.2 #2540 (SPIKE)	.54	7.58	.79	ND	.03	8.95	2.9	.13
4 Ch + 0.2 #2540	.07	ND	ND	.07	.03	1.15	2.7	.13
5 Ch + 0.2 #2540 (SPIKE)	.59	7.38	.79	.05	.03	9.95	3.0	.14
6 Ch + 0.2 #2540	ND	.01*	ND	ND	.03	.35	2.7	.12
5 Ch + 1 M.S.	.03	0.02	ND	.04*	.03	.85	3.0	.13
5 Ch + 2 M.S.	ND	ND	ND	ND	.03	.35	3.0	.12
5 Ch + 1 M.S. + 0.2 #2540	ND	ND	ND	ND	.03	.45	3.1	.13
5 Ch + 2 M.S. + 0.2 2540	.08	ND	ND	ND	.03	1.05	2.7	.13
20 Alum + 2 M.S	.10	.04	ND	1.58	.03	1.45	3.0	.14
20 Alum + 2 Ch	.03	.03	ND	1.28	.03	.85	3.0	.13

Note: Ch = chitosan, M.S. = moringa stenopetala, 2540 = anionic polyacrylamide of 40 mole charge percent,
* = at detection limit; ND = non-detect.

APPENDIX G
METALS % REMOVAL DATA
JUNE 17, 1992

Chemical Regime (Coagulant Conc. in mg/L)	Cr % Rem.	Zn % Rem.	Cu % Rem.	Al % Rem.	Ba % Rem.	Fe % Rem.	Si % Rem.	Mn % Rem.
20 FeCl ₃ +0.2 #2540	65	50	93	68	40	30	9	(-)
40 FeCl ₃ +0.2 #2540	66	ND	83	68	20	11	0	(-)
20 Alum+0.2 #2540	100	ND	100	(-)	40	99	(-)	55
40 Alum+0.2 #2540	100	ND	ND	(-)	40	100	18	55
10 FeCl ₃ + 2 Ch	96	ND	86	50	40	41	3	(-)
15 FeCl ₃ + 2 Ch	98	63	97	100	40	74	9	(-)
20 FeCl ₃ + 2 Ch	100	63	ND	86	60	85	9	(-)
25 FeCl ₃ + 2 Ch	91	50	100	45	40	(-)	0	(-)
30 FeCl ₃ + 2 Ch	94	ND	ND	82	40	30	12	(-)
30 FeCl ₃ + 2 Ch + 0.2 #2540	100	ND	ND	100	40	93	21	(-)
10 FeCl ₃ + 2 M.S.	95	ND	100	55	40	25	12	(-)
15 FeCl ₃ + 2 M.S.	91	ND	28	77	40	38	12	(-)
20 FeCl ₃ + 2 M.S.	100	100	ND	36	40	49	12	(-)
25 FeCl ₃ + 2 M.S.	100	ND	ND	73	40	68	9	(-)
30 FeCl ₃ + 2 M.S.	ND	ND	ND	ND	ND	ND	ND	ND
30 FeCl ₃ + 2 M.S.+ 0.2 #2540	ND	ND	ND	ND	ND	ND	ND	ND
1 Ch + 0.2 #2540	ND	ND	ND	ND	ND	ND	ND	ND
2 Ch + 0.2 #2540	ND	ND	ND	ND	ND	ND	ND	ND
3 Ch + 0.2 #2540 (SPIKE)	50	(-)	(-)	86	40	(-)	12	55
4 Ch + 0.2 #2540	94	100	100	68	40	68	18	55
5 Ch + 0.2 #2540 (SPIKE)	45	(-)	(-)	77	40	(-)	9	52
6 Ch + 0.2 #2540	100	88	100	100	40	90	18	59
5 Ch + 1 M.S.	97	75	100	82	40	77	9	55
5 Ch + 2 M.S.	100	100	ND	100	40	90	9	59
5 Ch + 1 M.S. + 0.2 #2540	100	100	ND	95	40	88	6	55
5 Ch + 2 M.S. + 0.2 2540	93	ND	100	91	40	71	18	55
20 Alum + 2 M.S	91	50	100	(-)	40	60	9	52
20 Alum + 2 Ch	97	63	100	(-)	40	77	9	55

Note: Ch = chitosan, M.S. = moringa stenopetala, 2540 = anionic polyacrylamide of 40 mole charge percent.
(-) means a negative % removal.

BATCH TEST PROCEDURE FOR PAH TESTING AT DEER ISLAND

PAH testing of samples taken at Deer Island for coagulant and flocculent testing requires the use of 10 gallon plastic or metal containers mixed by a stirrer driven by an electric power drill. The speed control mechanism of the drill is not precise; only slow, medium and fast speed delineations can be made. The following procedure should be followed to simulate jar test mixing conditions.

1. Using an indelible marker, note the water level on the container's inner wall corresponding to 30 liters (7.9 gal). Use this mark as a reference for future samples.
2. Fill the container with 30 liters (7.9 gal) raw sample water.
3. Mount the wooden drill holder, along with the drill, on top of the container so that the drill shaft is properly centered. (Note: Make sure the shaft is securely fastened to the drill).
4. Stir the raw sample for 30 seconds to make sure it is well mixed.
5. Using a syringe (or measuring pipette), add the test quantity of coagulant to the sample at the center of the container. (Avoid adding the coagulant directly on the stirrer; improper dosage may result).
6. Mix for 30 seconds at high speed (approximately 100 rpms).
7. Reduce stirrer to medium speed (approximately 60 rpms) and mix for 2 minutes. If a coagulant aid is also used, add at half-way point (i.e., after 1 minute). Mix at high speed (100 rpms) for 10 seconds, and then resume medium speed (60 rpms) for remainder for 2 minutes.
8. If a flocculent is used, add flocculent and mix at high speed (100 rpms) for 10 seconds.
9. Reduce to slow speed (20 rpms) and mix for 2 additional minutes.
10. Stop all mixing and allow 20 minutes for floc to settle.
11. Decant 17.1 liters (4.5 gallons) into cleansed 1-gallon bottles.
12. Repeat entire procedure once to obtain 34.2 liters (9 gallons) PAH sample.

Appendix

H

Batelle PAH Data from Deer Island Influent and Effluent

	Raw Inf.	Raw Inf.	Raw Inf.	Ave Inf.	Raw Eff.	Raw Eff.	Raw Eff.	Ave Eff.	Ave. %
	11/13/91	11/14/91	11/15/91	Nov-91	11/13/91	11/15/19	11/15/91	Nov-91	Removal
naphthalene	2544	4283	2687	3171	1472	2692	1325	1830	42
acenaphthylene	23	36	37	32	16	14	15	15	53
acenaphthene	ND	ND	ND	ND	ND	ND	ND	ND	ND
fluorene	382	680	862	641	203	275	175	218	66
phenanthrene	541	839	1248	876	327	317	283	309	65
anthracene	43	87	58	63	27	28	27	27	56
methylp + methylan	208	271	586	355	110	101	95	102	71
fluoranthene	171	344	228	248	123	102	102	109	56
pyrene	182	350	302	278	121	105	104	110	60
methylfl. + methylpyrene									
benz[a]anthracene	58	126	77	87	39	33	34	35	59
chrysene	63	142	91	99	45	39	40	41	58
benzo[b] + benzo[k]	80	174	100	118	58	42	43	48	60
benzo[a]pyrene	37	84	44	55	23	18	18	20	64
benzo[e]pyrene	36	72	45	51	23	18	21	21	59
benzo[ghi]perylene	21	49	22	31	16	12	11	13	58
indeno[1,2,3-cd]pyrene	29	51	33	38	20	18	21	20	48
dibenz[a,h]anthracene	3	9	4	5	3	2	2	2	56

November, 1991

Appendix H -- PAH Raw Influent Results

m/e	COMPOUNDS	4/21/92	6/12/92	6/12/92	Average
		Influent	Influent	Influent	Influent
			#1	#2	
			Sample	Sample	
		ng/l	ng/l	ng/l	ng/l
128	naphthalene	5.62	3.31	118	42.31
152	acenaphthylene	4.02		7.88	5.95
154	acenaphthene	5.96		16.9	11.43
166	fluorene	48.12	2.11	35.2	28.48
178	phenanthrene	62.12	3.33	46.2	37.22
	anthracene	5.65	0.12	5.64	3.80
192	methylphenanthrene +		5.45	76.6	41.03
	methlanthracene				
202	fluoranthene	29.68	1.21	18.2	16.36
	pyrene	25.25	0.83	17.9	14.66
216	methylfluoranthene		2.77	42.6	22.69
	methylpyrene				
228	benz[a]anthracene	9.9	0.01	3.9	4.60
	chrysene	11.88	2.12	7.41	7.14
252	benzo[b]fluoranthene +	15.88	0.52	5.29	7.23
	benzo[k]fluoranthene				
	benso[a]pyrene	1.24	0.17	1.38	0.93
	benso[e]pyrene		0.53	1.62	1.08
276	benzo[ghi]perylene +	47.7		1.06	24.38
	indeno[1,2,3-cd]pyrene			0.98	0.98
278	dibenz[a,h]anthracene	12.01		0.13	6.07

Appendix H -- PAH Effluent Results

m/e	COMPOUNDS	7/27/92	7/27/92	7/27/92	8/12/92	7/27&8/12
		Effluent	Effluent	Average	Effluent	Average
				Effluent		Effluent
		1st Run	2nd Run	Run 1+2		
		ng/l	ng/l	ng/l	ng/l	ng/l
128	naphthalene	2619	2153.2	2386	4116	3251
152	acenaphthylene	98.9	80.4	90	886	488
154	acenaphthene	195	240.7	218	3810	2014
166	fluorene	199	248.61	224	10205	5214
178	phenanthrene	299	325.6	312	261	287
	anthracene	17	21.53	19		19
192	methylphenanthrene +	180	217.11	199		199
	methlanthracene					
202	flouranthene	121	128.09	125	3719	1922
212	pyrene	124	138.57	131	23566	11849
216	methylfluoranthene	41.7	52.3	47		47
	methylpyrene					
228	benz[a]anthracene		28.82	29	1287	658
	chrysene		50.72	51	13729	6890
252	benzo[b]fluoranthene +		33.67	34	1977	1005
	benzo[k]fluoranthene					
	benso[a]pyrene		32.57	33	2652	1342
	benso[e]pyrene		41.81	42	6408	3225
276	benzo[ghi]perylene +					
	indeno[1,2,3-cd]pyrene					
278	dibenz[a,h]anthracene					

Appendix H -- Complete PAH Test Results

m/e	COMPOUNDS	6-Jul FeCl3 + #2540 ng/l	27-Jul Effluent	27-Jul Effluent 2nd Run ng/l	27-Jul Average Effluent 2nd Run ng/l	27-Jul FeCl3 + chitosan 1st Run ng/l	27-Jul FeCl3 + chitosan 2nd Run ng/l	27-Jul Average FeCl3 + chitosan ng/l	27-Jul % Improvement ng/l	12-Aug Effluent ng/l	12-Aug FeCl3 + #2540 ng/l	12-Aug % Improvement ng/l
128	naphthalene	112.6	2619	2153.2	2386	165	457.6	111	87	4116	1738	58
152	acenaphthylene		98.9	80.4	90	6.46	46.47	26	70	886		
154	acenaphthene	18.47	195	240.7	218	18.6	95.61	57	74	3810	736	81
166	fluorene	3.85	199	248.61	224	23.8	171.7	98	56	10205	2087	80
178	phenanthrene	62.2	299	325.6	312	73.9	267.5	171	45	261	4656	1684
	anthracene	1.69	17	21.53	19	4.69	24.13	14	25		188	
192	methylphenanthrene +	198.05	180	217.11	199	31.1	182.41	107	46		9936	
	methlanthracene											
202	fluoranthene		121	128.09	125	35.8	285.81	161	29	3719	300	92
212	pyrene		124	138.57	131	34.9	175.22	105	20	23566	5152	78
216	methyfluoranthene		41.7	52.3	47	23.2	90.42	57	21		15232	
	methyipyrene											
228	benz[a]anthracene			28.82	29	1.33	57.58	29	29	1287	3422	166
	chrysene			50.72	51	10.8	60.73	36	29	13729	1022	93
252	benzo[b]fluoranthene +			33.67	34	9.6	44.28	27	20	1977	366	81
	benzo[k]fluoranthene											
	benzo[a]pyrene			32.57	33	7.1	59.28	33	29	2652	411	85
	benso[c]pyrene			41.81	42	6.73	37.97	22	47	6408	1069	83
276	benzo[ghi]perylene +											
	indeno[1,2,3-cd]pyrene											
278	dibenz[a,h]anthracene						31.9	32	31		Average	-102

APPENDIX H
PAH ANALYSIS PROCEDURE

1. Add 1 ml of the internal standard, 1 ug/ml pyrene-d10 to each 1 gallon water sample.
2. Extract each 1 gallon water sample with 100 ml toluene. Let the separatory funnels sit for 10 minutes. Collect the extract in a 500 ml round-bottom flask.
3. Repeat 2 twice.
4. Evaporate the extract with Rotavapor to less than 50 ml.
5. Transfer the extract to a 50 ml pear-shaped flask. Evaporate it with Rotavapor to about 1 ml.
6. Run the extract through a silica column (100-200 mesh 5% deactivated silica).
 - 1st elution: with 30 ml of hexane. Collect the solution in a 50 ml pear-shaped flask -> fraction #1.
 - 2nd elution: with 30 ml hexane + toluene (3+1) -> fraction #2.
 - 3rd elution: with 30 ml hexane + toluene (1+1) -> fraction #3.
7. Evaporate fraction #2 with Rotavapor to a few milliliters.
8. Transfer the extract to a scaled 15 ml centrifuge tube.
9. Blow down the extract with nitrogen (or argon) to 0.2 ml.
10. Add 2 ul of the second internal standard, 100 ug/ml 1,1'-binaphthyl, into the extract.
11. Inject 1 ul of the extract into the gas chromatograph-mass spectrophotometer (GC-MS). GC-MS temperature program: 100-300 degrees Celsius at 5 degrees/minute.

APPENDIX I
BACKGROUND ECONOMIC INFORMATION
ON THE UNITED STATES AND GLOBAL CHEMICAL COAGULANT MARKET

The market for water and wastewater treatment chemicals has been growing at 6% to 9% from 1987 - 1992 and exceeds \$6 billion worldwide. Coagulants and flocculants for treating municipal and industrial wastewaters and for potable water are the most dynamic sector of the market. The industry is driven by increasingly stringent environmental regulations (Donaldson, J. 1992).

Quantities Used:

Metal Salt Coagulants: In 1978, about 400,000 metric tons of inorganic coagulants were used in the United States and about 150,000 metric tons in Western Europe, in both cases almost exclusively for water treatment. Alum enjoys the largest market share.

Synthetic organic coagulants/flocculents (calculated as dry mass): In 1984, the use of synthetic organic coagulants/flocculents in the United States was about 40,000 metric tons, half of this being accounted for by polyacrylamides. In Western Europe, about 15,000 metric tons were used. Large markets also exist in Canada, South America, Africa, Australia, and Japan (Gerhartz, W. 1988). [Currently, 15-20 main suppliers in the world produce in excess of 45,000 English tons/yr of polyacrylamides (Grayson, 1982). The U.S. International Trade Commission reported U.S. production to be 27,000 British tons (Grayson, 1982)]

Metal Salt Costs:

Metal salt costs range from \$.10 - \$.25/lb. The various costs are given in Table I-1. All costs are given on a dry basis.

TABLE I-1
COST COMPARISON OF VARIOUS METAL SALTS

Chemical	Cost (\$/lb)	Cost (\$/kg)
Alum	.10	.22
Ferric chloride	.10	.22
Aluminum chloride	.15	.33
Polyaluminum chloride	.25	.55

Polymer Costs:

1981 prices of polyacrylamides were \$1.77 - \$3.72/lb (\$3.89 - \$8.18/kg) on a polymer basis. Generally, cationics

command the highest price of \$2.04 - \$3.72/lb (\$4.48 - \$8.18/kg). High molecular weight anionics cost \$1.77 - \$2.95/lb (\$3.68 - \$6.48/kg). Because polyacrylamides are petrochemically based, their cost is tied to the price of fossil fuels and can be expected to rise accordingly.

1992 chitosan costs range from \$3.50 - \$6.00/lb (\$7.70 - \$13.00/kg).

Table I-2 summarizes these costs. All costs are given on a dry basis.

TABLE I-2
COST COMPARISON OF POLYACRYLAMIDES AND CHITOSAN

Chemical	Cost (\$/lb)	Cost (\$/kg)
Cationic polyacrylamide	2.04 - 3.72	4.48-8.18
Anionic polyacrylamide	1.77 - 2.95	3.68-6.48
Chitosan	3.50 - 6.00	7.70 - 13.00

Table I-3 lists the costs of other natural polymers.

**TABLE I-3
NATURAL POLYMER COSTS**

Type	Polymer	Cost (\$/kg)
Natural	agar	12.67 - 14.87
	casein	1.60 - 1.75
	corn starch	0.17 - 0.18
	guar gum	0.99 - 1.76
	gum arabic	1.58 - 2.53
	gum tragacanth	18.73 - 74.90
	karaya gum	3.30 - 3.75
	locust bean gum	2.31 - 2.42
	pectin	16.96
	sodium alginate	4.08 - 7.71
	xanthan gum	6.37 - 8.82
Modified Natural	cationic starches	
	gelatin	2.09 - 2.42
	hydroxyethyl cellulose	3.37 - 6.17
	methyl cellulose	3.37 - 4.63
	sodium carboxymethyl cellulose	1.68 - 2.54
	sodium carboxymethyl starch	

(1979 Prices, Grayson, 1982)

Tables I-4 gives representative worldwide producers of inorganic coagulants, Table I-5 gives the major producers of synthetic organic flocculents, and Table I-6 lists some of the polyacrylamides commercially available in the United States.

TABLE I-4
REPRESENTATIVE WORLDWIDE PRODUCERS OF INORGANIC COAGULANTS

COAGULANT	PRODUCER
Alum	Allied (USA)
	American Cyanamid (USA)
	Kemira Kemwater [Boliden?] (Sweden)
	Giulini Chemie (FRG)
	Stauffer (USA)
	Nikkei Kako (Japan)
	Scintoma Aluminum Smelting (Japan)
Polyaluminum chloride	Giulini Chemie (FRG)
	Sachteben Chemie (FRG)
Sodium Aluminate	Giulini Chemie (FRG)
	Nalco Chemical (USA)
Iron (III) chloride	BASF (FRG)
	Dow Chemical (USA)
	Pennwalt (USA)
	Solvay (Switzerland)
Iron (III) sulfate	Giulini Chemie (FRG)
Iron (III) sulfate chloride	Kronos Titan (FRG)
Iron (III) sulfate	Kronos Titan (FRG)
	Pfizer (USA)
	Societe des Fabriques de Produits Chimiques de Thann et Mulhouse (France)
Sodium silicate	Allied (USA)
	Solvay (Belgium)
	Wollner-Werke (FRG)

TABLE I-5
PRIMARY WORLDWIDE PRODUCERS OF SYNTHETIC ORGANIC FLOCCULENTS

PRODUCER	FLOCCULENT
Allied Colloids (UK)	Magnafloc, Percol, Zetag
American Cyanamid (USA)	Superfloc, Accurac
BASF (FRG)	Sedipur, Polymin
Betz Laboratories (USA)	Polyfloc, Betz
Calgon (USA)	Calgon, Hydraid
Chemische Fabrik Stockhausen (FRG)	Praestol
Dow Chemical (USA)	Separan, Purifloc
Hercules (USA)	Hercofloc, Reten
Kurita Kogyo (Japan)	Kurifloc
Mitsubishi Chemical (Japan)	Diaclear
Nalco Chemical (USA)	Nalco
Rohm (FRG)	Rohafloc
Sankyo Chemical (Japan)	Sanpoly
Sanyo Chemical (Japan)	Sanfloc
Societe Nationale de Flocculant (France)	Floerger

TABLE I-6
SOME ANIONIC AND CATIONIC POLYACRYLAMIDES
AVAILABLE IN THE UNITED STATES

Trade Name	Ion Type	Manufacturer
Aerofloc 550	anionic	American Cyanamid Co.
Gafloc	cationic	GAF Corp.
Hercofloc 816-823	anionic	Hercules, Inc.
Hydroaid 776	cationic	Merck & Co.
Magnifloc 521C, 523C	cationic	American Cyanimid Co.
Nalco 633	anionic	Nalco Chemical Co.
Polyfloc 1260	cationic	Betz Laboratories, Inc.
Polyhall 295	anionic	Stein Hall and Co.
Reten 205, 210	cationic	Hercules, Inc.
	cationic	Delta Chemicals
	anionic	Delta Chemicals
Separan CP7	cationic	Dow Chemical Co.
Separan NP10	anionic	Dow Chemical Co.

The largest application of anionic polyacrylamides is as a flocculent in wastewater clarification of municipal sewage, industrial plants and mining (Grayson, 1982). An important use for cationic polyacrylamides is for sewage sludge dewatering (Grayson, 1982)

Natural Organic Polymers

Due to their low relative molecular masses ($10^3 - 10^5$), these polymers as a class are only moderately efficient. Despite the very low cost of some of these natural products, the cost-to-performance ratio of synthetic flocculants is considerably more favorable due to their very high relative molecular masses ($10^5 - 20 \times 10^6$). Consequently, natural organic polymers have steadily declined in importance. Only water-soluble starch has been able to maintain its market position in certain fields for any length of time, e.g. in the purification of wastewater. Starch was chosen in wastewater applications because, unlike synthetic organic polymers, its use did not require legal permission (Gerhartz, 1988).

Key U.S. producers of natural polymers are given in Table I-7.

